

THE NITRATION AND FRACTIONATION  
OF  
WHOLE WOOD

by

WILMA ETHEL ELIAS

B.A. (Hons.), University of Saskatchewan, 1947  
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THE REQUIREMENTS FOR THE DEGREE OF  
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in the Department

of

Chemistry

We accept this thesis as conforming to the  
required standard.

THE UNIVERSITY OF BRITISH COLUMBIA

October, 1956

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Department of Chemistry

The University of British Columbia,  
Vancouver 8, Canada.

Date Oct. 15, 1956.

# The University of British Columbia

Faculty of Graduate Studies

## PROGRAMME OF THE FINAL ORAL EXAMINATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

*of*

WILMA ETHEL ELIAS

B.A. (Saskatchewan), 1947

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MONDAY, OCTOBER 15th, 1956, at 11:30 a.m.

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McGill University

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The crystalline compounds D-mannitol, benzoic acid and D,L-tartaric acid were smoothly nitrated by exposure to an excess of the pentoxide at  $0 \pm 2^{\circ}\text{C}$ . and the crystalline products D-mannitol hexanitrate, D,L-tartaric acid dinitrate and *m*-nitrobenzoic acid were recovered directly in quantitative yield. Good yields of the crystalline although somewhat less pure nitrates of D,L-mandelic acid, *B*-methyl-D-glucopyranoside and D-sorbitol were obtained in similar nitration. D-Mannose, D-fructose, dulcitol, sucrose, maltose, lactose, cellobiose, vanillic acid, salicylic acid and vanillin gave poor yields of syrupy nitrated products.

A beechwood xylan and holocellulose and lignin of western red cedar, isolated by conventional technics, were nitrated by the gaseous pentoxide method in yields and nitrogen contents comparable to those reported for other nitration methods. The xylan and holocellulose nitrates were incompletely soluble in acetone and the solubility of the nitrated lignin varied with the time of nitration.

Optimum conditions were established for the nitration of acetone-extracted western red cedar heartwood. The weight ratio of nitrated wood : wood was closely reproducible and exceeded previously reported values; total nitrogen and ester nitrogen contents of the nitrated wood were reproducible within the experimental error of the determinations. The nitration reaction was not entirely quantitative since an average of 2.3% methoxyl was lost from the wood and the weight increase calculated from the total nitrogen content was, on the average, 3% lower than the observed value.

Successive extraction with anhydrous acetone and methanol applied alternately, dissolved up to thirty-five percent of the nitro-wood and indicated that the nitration-solvent extraction technic should have value as a tool in the study of wood chemistry.

## GRADUATE STUDIES

### Field of Study: Chemistry

Statistical Mechanics.....	Dr. J. G. Hooley
Stereochemistry.....	Dr. L. D. Hayward
Conjugated Systems and Aromatic Character.....	Dr. G. G. S. Dutton
Cellulose, Lignin and Related Compounds.....	Dr. L. D. Hayward
Organic Seminar.....	Dr. G. G. S. Dutton
Molecular Rearrangements.....	Dr. A. Rosenthal

### Other Studies:

Wave Mechanics.....	Dr. G. M. Volkoff
Research in Wood Anatomy.....	Mr. J. W. Wilson
Seminar in Biochemistry.....	Dr. S. Zbarsky

### Outside Interest: Music.

*chris*

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**I. INTRODUCTION**

Relatively little is known about the hemicellulose fraction of wood or other plant materials, so that any investigation of the structure of these polymeric substances would be both interesting and profitable. However, before such a study can be undertaken, the component in which one is interested must be separated from the others present--lignin and cellulose in the case of wood. Furthermore, in order that structural studies may yield useful information concerning the state of the component in situ, the physical and chemical changes which it has undergone during the separation must be of a known and reproducible nature. This situation, unfortunately, represents an ideal case which is seldom attained in practice.

One common method of separation involves conversion of the crude material, e.g., whole wood, to a suitable derivative, followed by subjection of the organic-solvent soluble material to an elaborate process of fractional solution or fractional precipitation, or to a combination of both. The derivatives of carbohydrate polymers most often chosen are the methyl ethers or the acetate or nitrate esters. All common methods for the formation of the former two derivatives require drastic conditions, result in incomplete substitution and lead to chain and unit degradation. In the formation of nitrate esters, the products are often oxidized, hydrolyzed or incompletely substituted. In cases where the greater number of these disadvantageous side reactions have been avoided, solubility properties of the nitrated material are often unsatisfactory and, when a liquid nitrating reagent is used, loss of a portion of the product to the solution medium is inevitable. Despite all these

disadvantages, however, the nitrate ester derivatives seem to be the most suitable on which to conduct fractionation studies of carbohydrate-containing natural products.

When interest is centred on a component such as hemicellulose, which is very closely associated with both the lignin and cellulose fractions of wood, it is imperative that the fate of the total material be known. For this reason, it seemed desirable to investigate the use of a gaseous nitrating agent. Dinitrogen pentoxide was chosen because of its great reactivity as a nitrating reagent and because it had been shown not to cause degradation of carbohydrate polymers. The work reported in this thesis covers an investigation of the reaction of this reagent with western red cedar heartwood and preliminary studies on the solubility of the nitrated wood produced.

The nitration of wood itself was preceded by studies on model compounds under conditions similar to those eventually used with the wood.

Western red cedar (Thuja plicata) was chosen as the starting material because of its special interest to British Columbia where, as in the states of Washington and Oregon, it is one of the important forest species.

**II. HISTORICAL SURVEY**

## A. THE NITRATION REACTION

### 1. INTRODUCTION

In compiling the information for this section, the following considerations have prevailed.

With very few exceptions, the survey of theoretical work has been concerned only with papers appearing in recent years. Early work on the mechanism of nitrations has been reviewed by several authors (33, 148, 213).

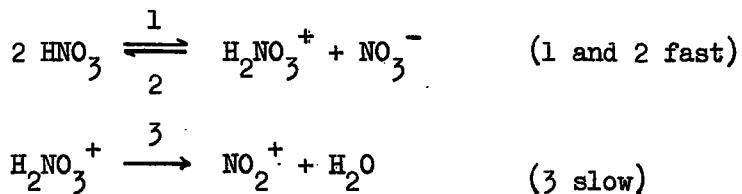
In order to facilitate comparison with previously reported work, it seemed essential to include a brief but reasonably comprehensive survey of the reactivities of a number of nitrating agents and the nature of the nitration products formed from various starting materials. (The nitration of plant tissues has not previously been reviewed.) The major interest, for the purpose of this thesis, was in nitrations which were carried out in the absence of water. For this reason, the discussion of sulfonitric mixtures (which usually contain some water) has been severely curtailed.

It was also felt that a brief description of the structure of whole wood would further facilitate the understanding of its behaviour towards various nitrating agents. This is followed by a survey of the nitration of components isolated from wood, with the exception of cellulose which has been considered in some detail in connection with the reactivities of nitrating agents. Finally, reported work on the nitration of wood itself is summarized.

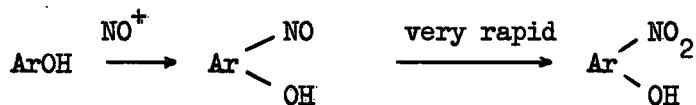
A brief survey of the nitration of the model compounds studied during the course of the present work is also included.

## 2. THE MECHANISM OF NITRATION

As early as 1903 it was postulated that the nitronium ion ( $\text{NO}_2^+$ ) was the active agent in most nitrating mixtures (122). From time to time thereafter, similar proposals were made (for example see ref. 304 and the review papers 33, 148, 213). However, it was not until 1946 that positive proof of the existence of such an ion was obtained (148). Now, evidence from four sources—cryoscopic measurements and spectroscopic analyses of nitrating mixtures, and spectroscopic and X-ray analyses of nitronium salts—offers further proof of the existence of nitronium ions. The nitronium ion is considered to be formed from nitric acid (147, 208b) according to the following equations:

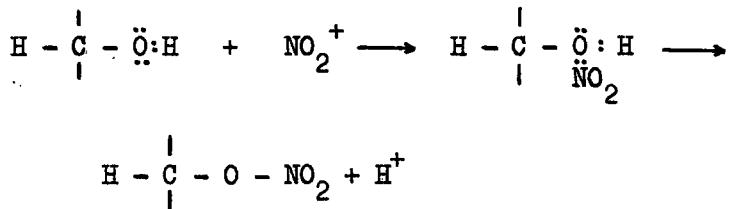


It has since been shown that the nitronium ion is the active agent both in N-nitrations (43) and in C-nitrations (213) of many aromatic compounds of intermediate reactivity. Reactive compounds such as phenols and amines react by a different mechanism—the so-called "special mechanism" (64). The reactive agent here is the nitrosonium ion ( $\text{NO}^+$ ) which first substitutes on the ring and then is quickly oxidized to a nitro ( $-\text{NO}_2$ ) group.



Shortly after establishment of the nitronium ion mechanism for C-nitrations, Israelashvili (216) postulated that O-nitration would

be expected to occur in the same manner. This conclusion was prompted by noting that starch was nitrated most effectively by reagents in which large concentrations of nitronium ion were known to exist.



Blackall and Hughes (43) have proved, by means of kinetic studies, that O-nitration of simple alcohols does occur through attack by the nitronium ion. On the basis of their work with simple aliphatic alcohols and preliminary experiments with glycerol and cellulose, these authors believe that the nitronium ion mechanism is responsible for all O-nitrations.

Klein and Mentser (235) also claim to have established the validity of the nitronium ion mechanism through their work on the nitration of cellulose with sulfonitric mixtures containing  $\text{O}^{18}$  - enriched nitric acid. Only two of the three oxygen atoms in each nitrate group of the nitrocellulose showed enrichment of their  $\text{O}^{18}$  content.

### 3. NITRATING REAGENTS

Gillespie and Millen (148) list the following nitrating agents in order of their increasing strength:

ethyl nitrate — nitric acid — acetyl nitrate — dinitrogen pentoxide — nitryl chloride — nitracidium ion — nitronium ion

Of the reagents mentioned, nitric acid, either alone or in solution, is by far the most commonly used. Solvents affect the speed and often, also, the course of the reaction. Hughes, Ingold and Reid (208b) give the following graded series of solvents; those at the left greatly accelerate the rate of nitration, those at the right decrease the rate.

sulfuric acid > nitric acid  $\gg$  nitromethane > acetic acid  $\gg$  water

Fast medium slow

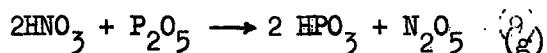
This is in agreement with the earlier suggested series of Benford and Ingold (31) who include dioxane in the slow and acetic anhydride in the medium solvents.

The reactive species considered to be present in various nitrating agents are listed in Table I. In the earlier literature, the  $1400\text{ cm}^{-1}$  line of the raman spectrum was considered to be characteristic of dinitrogen pentoxide. It has since been assigned to the nitronium ion, and the data collected in Table I have been reinterpreted to correspond to this more recent assignment.

Evidence (94, 159, 161, 215) indicates that the nitronium ion is linear in structure.

#### 4. DINITROGEN PENTOXIDE

(a) Preparation.- Dinitrogen pentoxide is most conveniently and most commonly prepared from a mixture of anhydrous nitric acid



and phosphorus pentoxide (146, 153, 306). It is interesting to note

TABLE I  
The Constitution of Common Nitrating Agents

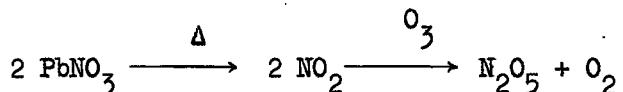
Nitrating Agent	Active Species	Evidence (1)	Reference
HNO <sub>3</sub> (anhyd.)	NO <sub>2</sub> <sup>+</sup>	S K	226 208b
	NO <sub>2</sub> <sup>+</sup>	C	146
		Ch	396
HNO <sub>3</sub> /H <sub>2</sub> O up to 12% H <sub>2</sub> O	NO <sub>2</sub> <sup>+</sup> (NO <sub>2</sub> <sup>+</sup> ) (NO <sub>2</sub> <sup>+</sup> )	S K Ch	146, 226 208b 396
	H <sub>2</sub> NO <sub>3</sub> <sup>+</sup>	S, K	171
HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	NO <sub>2</sub> <sup>+</sup>	(2)	33, 148, 213, 282
		E	33
		C	144, 145
		S	79a, 141, 289a
		K	47
HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O	NO <sub>2</sub> <sup>+</sup>	E	267
HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> /SO <sub>3</sub>	NO <sub>2</sub> <sup>+</sup>	S	79c,d, 215
		Ch	50
	NO <sub>2</sub> <sup>+</sup> in all mixtures studied	E	33
HNO <sub>3</sub> /H <sub>2</sub> SeO <sub>4</sub>	NO <sub>2</sub> <sup>+</sup>	S	215
HNO <sub>3</sub> /HClO <sub>4</sub>	NO <sub>2</sub> <sup>+</sup>	S	215
HNO <sub>3</sub> /P <sub>2</sub> O <sub>5</sub>	NO <sub>2</sub> <sup>+</sup>	S	79a, 226

- (1) The following symbols are used: S, spectroscopic; K, kinetic;  
C, cryoscopic; Ch, chemical; E, electrolytic; X, x-ray  
measurements, as the source of evidence.
- (2) Evidence gathered from a survey of the literature.

Table I (contd.)

$\text{HNO}_3/(\text{CH}_3\text{CO})_2\text{O}$	$\text{NO}_2^+$ $\text{CH}_3\text{CO}\cdot\text{ONO}_2^+, \text{N}_2\text{O}_5$ or $\text{NO}_2^+$	S Ch K S E K	226 270, 278 152 80 383b 208a
$\text{HNO}_3/\text{CH}_3\text{CO}_2\text{H}$	$\text{NO}_2^+$	E	383b
$\text{HNO}_3/\text{CH}_3\text{NO}_2$	$\text{NO}_2^+$	K	208b
$\text{N}_2\text{O}_5$ cryst.	$\text{NO}_2^+$	X S	226
gas.	$\text{N}_2\text{O}_5$	S	153
inorg. solvents	$\text{N}_2\text{O}_5$	K	153
oleum	$\text{NO}_2^+$	E	33
$\text{N}_2\text{O}_5/\text{HNO}_3$	$\text{NO}_2^+$	S	214
		K	153
		C	146
$\text{N}_2\text{O}_5/\text{H}_2\text{SO}_4$	$\text{NO}_2^+$	K C S	145, 151a, 153 289b
$\text{N}_2\text{O}_5/\text{H}_2\text{SO}_4/\text{SO}_3$		S	79c
benzoyl nitrate	$\text{N}_2\text{O}_5 + \text{C}_6\text{H}_5\text{CO}\cdot\text{ONO}_2$	K	152
$\text{C}_2\text{H}_5\text{ONO}_2/\text{H}_2\text{SO}_4$	$\text{NO}_2^+$	Ch	411

that Daniels (100) preferred to prepare dinitrogen pentoxide by subjecting nitrogen dioxide to the oxidizing action of ozone.



This was claimed to give a product free from the traces of moisture which might be present in the former mixture.

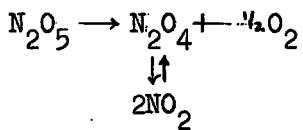
(b) Properties.- Dinitrogen pentoxide is a colorless solid which sublimes without melting (362) although liquid dinitrogen pentoxide has been prepared (9). It has a vapor pressure of one atmosphere at 32.5° C., and begins to melt at 41° C. Vapor pressures of the solid are shown in Table II.

TABLE II

The Vapor Pressure of Solid Dinitrogen Pentoxide (347)

T (°C.)	P (mm.)	T (°C.)	P (mm.)
-33	2.3	10.5	132
-21	6.3	15	183
-10.7	18.6	25	420
0	51.5	30	620
-	-	32.5	760

Boiling occurs at 45° C., accompanied by decomposition to dinitrogen tetroxide (283). It is known that rapid decomposition of dinitrogen pentoxide to dinitrogen tetroxide occurs at any temperature above 0° C. The rate of decomposition is independent of



surface effects, catalysts, many foreign substances and is almost independent of the solvent used (138, 222). Decomposition is inhibited by the presence of ozone (375). The reaction of dinitrogen tetroxide with ozone to form dinitrogen pentoxide is both rapid and quantitative (100, 222, 223, 334). For this reason the distillation of dinitrogen pentoxide in a stream of ozone is a recommended method for purification (300, 306, 375).

(c) The Structure of Dinitrogen Pentoxide.-- There is much confusion in the early literature on structure studies of dinitrogen pentoxide. This has been caused by two effects: (a) the raman spectrum of the nitronium ion in mixtures of acetic or phosphoric acids with nitric acid was not recognized as such, but considered to be characteristic of dinitrogen pentoxide. (b) Dinitrogen pentoxide can exist in either of two molecular states. In some solvents the molecular state is the same as for the gaseous molecule. In other solvents the molecular state is the same as for the solid pentoxide.

In the gaseous state (323) and in solution in organic solvents such as carbon tetrachloride and chloroform, dinitrogen pentoxide exists in its covalent form (79b, 80, 100, 151b, 159, 161). The structure is assumed to be  $\text{O}_2\text{N} - \text{O} - \text{NO}_2$  (362). Solid dinitrogen pentoxide has been shown to exist in the ionic state (161) as it does also in solution in such polar compounds as nitric or sulfuric acids or phosphorus pentoxide (79b, 80, 151b, 159, 161, 375).

Evidence for the existence of ions in the solid state ( $\text{NO}_2^+ \text{NO}_3^-$  i.e., as nitronium nitrate) is strengthened by the recent preparations of other nitronium salts such as the perchlorate (94) and others (143, 151a, 289c). As a matter of interest it may be mentioned that nitronium salts are now being used on an industrial scale for the preparation of nitrating mixtures (109, 184, 418).

Ready interconversion of the ionic and covalent forms occurs in solution in acids of weak and medium strength. It is thus seen that dinitrogen pentoxide can exist in two molecular states at the same temperature, depending on the solvent.

#### B. SCOPE AND LIMITATIONS OF THE NITRATION REACTION

(Excepting the Nitration of Wood, which is Considered Later)

##### 1. MISCELLANEOUS NITRATING REAGENTS

(a) Nitryl Halides.— Although Gillespie and Millen (148) include nitryl fluoride in the class of powerful nitrating reagents, compounds of the type  $\text{X} - \text{NO}_2$  seem to have been little used in that capacity. Nitryl chloride (328b) and nitryl fluoride (190) react similarly with aromatic compounds. Highly reactive compounds such as phenols, amines and polynuclear aromatic molecules are destroyed (oxidation), and unreactive compounds such as nitrobenzene and benzoic acid are not nitrated. Only compounds of intermediate reactivity react in a manner suitable for synthetic purposes. Nitryl chloride reacts variously with olefins (328a), giving addition of the elements of chlorine, dinitrogen trioxide or dinitrogen tetroxide. Although the nitryl fluoride molecule has been shown to be

planar (110) and thus presumably would have good powers of penetration of polymeric material, its reaction with cellulose or wood has not been studied.

(b) Other Reactions.- A number of alkyl nitrates have been prepared by the reaction of silver nitrate with the corresponding alkyl halide (20) 84, 96, 180, 285). Also, the preparation of organic nitrates by treatment of epoxides with nitrogen dioxide (101b), dinitrogen tetroxide (330) or nitric acid (298) has been reported. For obvious reasons, these methods and reagents need not be considered further in connection with their possible use in the nitration of carbohydrate polymers.

## 2. MIXTURES OF NITRIC AND SULFURIC ACIDS

Mixtures of nitric and sulfuric acids with varying amounts of water are widely used for the commercial preparation of cellulose nitrate (288). However, the interest for this thesis is limited to a consideration of those nitrating agents which do not contain added water. Thus, only mixtures of concentrated or fuming nitric and sulfuric acids, hereafter referred to as sulfonitric mixtures, are considered in the following short discussion.

The reactions of sulfonitric mixtures with simple carbohydrates such as saccharic acids (244b), disaccharides (240, 402), mono-saccharides and their derivatives (128, 402), hexitols (279, 317, 388) and aliphatic alcohols (119, 390) have been studied. Although the reaction varies considerably with the compound, it was found that carbohydrate molecules with free reducing groups gave very poor

results (402), as did sucrose (340). On the other hand, hexitols (279, 317, 388) and other substituted carbohydrates (402) could be nitrated in excellent yield.

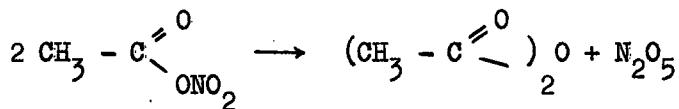
Sulfonitric mixtures have also been used extensively in the preparation of nitrates of polymeric carbohydrates. Materials such as cellulose (288), pectins (186), starch (54a, 288) and lichenin \* (369) have been converted to their nitrate esters by its use. However, there are many attendant disadvantages; the theoretical amount of nitrogen is never introduced (186, 369), extensive degradation generally occurs (174, 186, 369), sulfate groups are introduced (174), the products are often hard (hornified) and difficult to purify and stabilize (49b) and the rate of reaction is less than when other nitrating agents are used (71). The use of sulfonitric mixtures in organic solvents seems to overcome none of these difficulties (337). For these reasons recourse is generally made to other reagents when the object of preparing the nitrate esters is to form derivatives suitable for use in the study of the structure of the original polymer.

### 3. ACYL NITRATES

Although it has long been known that acyl nitrates are powerful nitrating agents, their manner of reaction is still unknown (65). Recent work has indicated (81, 152) that small amounts of dinitrogen pentoxide are formed by dissociation of acetyl nitrate, e.g.,

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\* Lichenin is a polymer of glucose, similar in structure to cellulose (324).



so that the active nitrating agent in the mixture might well be dinitrogen pentoxide rather than the nitrate.

Acetyl nitrate is the more commonly used of the two reagents whose nitrating action has been studied. With aromatic compounds its reaction has been found to differ from that of mixtures of nitric acid with acetic acid and/or anhydride in that the amount of dealkylation (of ethers) is less. For instance, both *o*- and *p*-nitro-anisole (65, 160) have been successfully prepared from anisole by its use. It has also been used to nitrate aromatic amines (202, 313b), anilides (313b), aromatic hydrocarbons (313b), benzoic acid (313b) and a variety of phenolic derivatives (314).

The reaction of acetyl nitrate with cellulose has also been reported. The results seemed to vary widely. Berl and Smith (39b) were able to produce a cellulose nitrate with a nitrogen content of 13.3%. (The nitrogen content of cellulose trinitrate is 14.14%.) By contrast, Chedin and Tribot (79g, 83d) found that this reagent had practically no effect on cellulose. Further investigation, however, revealed that the treatment which cellulose received prior to nitration had a marked effect on its ability to be nitrated, i.e., acetyl nitrate was not deficient as a nitrating agent but rather was deficient in its power to penetrate the cellulose structure. Chedin and Tribot (79g, 83d) were able to prepare a cellulose nitrate with a nitrogen content of 13.7% after pre-treatment of the cellulose in such a manner as to "open up" the

fibre. However, as will be shown later in the discussion, mixtures of nitric acid with acetic acid and acetic anhydride have a much stronger nitrating action on cellulose, so that the use of preformed acetyl nitrate is in no way advantageous in the preparation of cellulose trinitrate.

The action of benzoyl nitrate as a nitrating agent has also been studied. Its reaction with anisole is similar to that of acetyl nitrate (160). However, it was found to cause side chain substitution in durol (403) and to be less reactive in nitrating phenols than acetyl nitrate (314). Benzoyl nitrate functions as an oxidizing agent as well as a nitrating agent, although its reaction seems to be strongly governed by the nature of the compound. For instance, both vanillin and benzaldehyde were successfully nitrated, but anisaldehyde and salicylaldehyde were converted to the corresponding (nitrated) acids (129).

#### 4. NITRIC ACID

Although nitric acid containing small amounts of water is useful for the preparation of simple aliphatic nitrates (269) the anhydrous (fuming) acid is generally preferred for the nitration of polymeric carbohydrate materials. There are many attendant disadvantages to the use of fuming nitric acid, however. As early as 1895 Bader (16a, 16b) found that it was impossible to obtain a completely substituted product (xylan dinitrate) by the reaction of nitric acid with wood gum. With chitin \* (394) there was

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\* Chitin is a polymer of glucosamine which "... probably consists of continuous chains of N-acetylglucosamine residues connected through 1,4'- $\beta$ -glycosidic linkages ... extremely resistant to hydrolysis." (324).

obtained a mixture of nitrates which corresponded in properties to those of a cellulose nitrate (394) but nitration was accompanied by both oxidation and hydrolysis (88). Isolated pectins and pectins in situ reacted to give a product corresponding to the dinitrate (9.5% N) but here again the reagent caused degradation of the carbohydrate chains (186). Sulfonitric mixtures gave products which were less degraded, but also were not so highly substituted. Nitric acid seems to have been the preferred reagent for the preparation of pectin nitrates (45, 186, 254, 349, 367). Products with widely varying nitrogen contents have been isolated but, unfortunately, the results are not strictly comparable because of the many different sources of starting material.

The nitration of cellulose by fuming nitric acid has also been investigated. Although preparation of cellulose nitrates with nitrogen contents of up to fourteen percent has been reported (83c), it is now considered that the addition of inorganic salts to the nitrating acid is desirable. The nitrogen contents of the products are thereby increased, and the products are less brittle (49a, b, c). The choice of salt added was found to make little difference in the results. In no case was the theoretical amount of nitrogen introduced, a result which agreed with the earlier work of Rogovin and Paradyna (337). However, as with the other polymeric carbohydrates already mentioned, it has been found that oxidation also occurs (39a).

Results similar to those obtained with cellulose are reported for reactions of nitric acid with starch (37, 166).

It should be mentioned that reports in the early literature claiming high degrees of nitration of natural products must be inter-

preted with some caution. Berl and Rueff (38b) have pointed out that nitric acid is strongly adsorbed on both free hydroxyl and nitrate groups, which could result in fallacious values for the nitrogen contents of poorly-washed preparations.

Gaseous nitric acid is also an efficient nitrating agent. Although carbon-carbon bond cleavage has been reported in its reaction with simple alcohols (177) this does not seem to occur (at least to any <sup>appreciable</sup> extent) during the nitration of cellulose. With cellulose the amount of nitrogen introduced can be controlled by variation of the pressure and amount of gaseous nitric acid, the temperature and the time of reaction (49e, 63, 77, 338a, 385, 404). Products with nitrogen contents in the range 8.6 - 13.6% have been prepared. The less highly substituted cellulose nitrates were found to be less homogeneous than those of similar nitrogen content prepared with sulfonitric mixtures (77). X-ray studies, which allowed the course of reaction to be followed, showed that the surface of the fibre was first substituted to a high degree and only after this did the reaction penetrate to the interior.

Mixtures of anhydrous nitric acid with inert organic solvents have become almost standard for the preparation of the nitrate esters of simple carbohydrates and their derivatives (23, 108, 149, 237, 310, 311, 312). Yields are often quantitative. Such mixtures have, however, found only limited use in the nitration of cellulose. The nitration in carbon tetrachloride has been reported to occur with no degradation of the "fibre structure" (399a) but the nitrated cellulose produced was less soluble in organic solvents than that

treated with sulfonitric mixtures. A nitrate analyzing for fourteen percent nitrogen was obtained by treatment of cellulose with a solution of nitric acid in nitromethane (339). The reaction was accompanied by degradation.

Although nitrovanillin has been prepared from vanillin by use of nitric acid in ethereal solution (181), Gustaffson and Andersen (164) have recently shown that a side reaction, resulting in the production of dinitroquaiacol, also occurred.

A number of alkyl nitrates have been prepared by reaction of chloroform solutions of nitric acid with the corresponding alcohol (298).

Kurschner and his coworkers have used mixtures of anhydrous nitric acid and anhydrous ethanol (ethyl nitrate?) to nitrate a number of substances. The reaction with piperonal derivatives (248e), straw (248c), humic acids (248g, h, 252a) (which yield compounds not unlike nitrolignins) and wood (248j) has been studied.

##### 5. MIXTURES OF NITRIC ACID WITH ACETIC ACID AND/OR ANHYDRIDE

Reagents composed of varying proportions of nitric acid, acetic acid and acetic anhydride have been used for many years. That the mixtures are very active agents is shown by the successful nitration of compounds which ordinarily resist attack by electrophilic reagents. The reactions are often unique with respect to the products formed. This is indicated in their reaction with aromatic compounds, where the o/p ratios of the derivatives differ from those obtained by the use of other nitrating reagents (11, 321a).

In spite of their varying composition, all <sup>these</sup> mixtures possess approximately the same powers of nitration and will henceforth be referred to as acetonitric mixtures.

The nitrating action of solutions of nitric acid in acetic acid was discovered in 1902 by Pictet and Genequand (321a) who believed that they had established proof for the existence of a diacetyl nitric acid in the mixture. More recent work (124, 374) however, has shown that a molecular complex (nitric acid : acetic acid :: 1 : 1) is present and it has been suggested that the supposed compound reported by Pictet and Genequand was, in reality, an azeotrope. Be that as it may, these latter authors did establish that acetonitric mixtures can bring about acetylation and oxidation as well as nitration. It was also found that acetic acid is unique among organic acids in its power to form a useful nitrating reagent when mixed with nitric acid.

A wide variety of compounds has been successfully nitrated by use of suitable mixtures of acetic and nitric acids. These include: pyrazine derivatives (230) (the pyrazine nucleus is generally very resistant to attack by electrophilic reagents), carbohydrates (127, 206a), tropolones (91) and aromatic compounds (172, 383c, 416). The aromatic ring of a phenyl-glucoside was nitrated in both the ortho and para positions (264). On the other hand, acetonitric mixtures were found to be less suitable than sulfonitric mixtures for the nitration of phenazine (268). One disadvantage of the reagent is that it causes dealkylation (150, 262) and other degradative reactions (383c).

Its use in the production of cellulose nitrates with nitrogen contents of over fourteen percent has been reported (49a, d). It has been reported that stabilization of these high-nitrogen cellulose nitrates with ethanol resulted in the production of a cellulose nitrate with the theoretical 14.14% nitrogen (49d).

A mixture of nitric acid, acetic acid and trichloroacetic acid had been recommended as a reagent for the determination of crude cellulose in plant materials (389).

Mixtures of nitric acid and acetic anhydride are also useful nitrating reagents. The compounds nitrated by this mixture include guanidine (276), imidazoline derivatives (277), furfurylidine derivatives (348), thiophene (335), imides (231), carbamates (97), simple carbohydrates (206b, 361), high molecular weight alcohols and glycols (255) and aromatic compounds (160, 344). The aromatic compounds often formed derivatives the o/p ratios of which were different from the products of reaction with sulfonitric mixtures (11, 160). By contrast to the ready dealkylation reaction of nitric -acetic acid mixtures, nitric acid - acetic anhydride mixtures caused no dealkylation of butyl - substituted m-cresols (101a).

Mixtures of nitric acid and acetic anhydride permit the introduction of almost the theoretical amount of nitrogen into the cellulose molecule (49a). Chloroform or carbon tetrachloride solutions of these mixtures have also been used to nitrate cellulose, the content of nitrogen in the products being varied by the reaction conditions (53a, 101a, 399a).

Although mixtures of nitric acid and acetic anhydride are

convenient nitrating agents, their use is probably restricted to a certain extent by their explosive nature. It is known that the highly-explosive tetranitromethane is readily formed in such mixtures (78, 321b). Formation of tetranitromethane in no way detracts from the strength of these mixtures, as it itself is a powerful nitrating agent (167, 316). However, in the interests of safety, acetic acid is frequently added to nitric acid - acetic anhydride mixtures since its presence seems to hinder the formation of tetranitromethane (49b). This gives yet another series of acetonitric reagents--those containing both nitric and acetic acids as well as acetic anhydride. These mixtures are very similar in their reactions to those of acetic anhydride and nitric acid. They seem to be preferred for the preparation of highly-nitrated celluloses.

Hess and his coworkers (189) were not able to prepare cellulose nitrates with nitrogen contents in excess of 13.6% by use of these acetonitric mixtures. More recently, however, Bouchonnet, Trombe and Petitpas (49a, d) have prepared a cellulose nitrate the nitrogen content of which was in excess of fourteen percent. This value was raised to the theoretical 14.14% by suitable stabilization treatment. The direct preparation of cellulose trinitrate (i.e., without the need for stabilization) has been reported by Demougin (105) and by Bennett and Timell (39a, b). Cellulose nitrate is also prepared industrially by treatment with acetonitric mixtures (113). The cellulose nitrates resulting from treatment with these mixtures are superior to those prepared by other methods. They are less hard, brittle and agglutinized (384a) and are not degraded (32a, 174, 384b).

Nitrate derivatives of a large number of simple carbohydrates have been prepared by treatment with this reagent (53b, 126, 127, 206a, 246a). Nitration occurs almost instantaneously; yields are excellent and often quantitative. Simple alkyl nitrates have also been prepared in the same manner (25). By contrast, no nitrating action was evidenced with urethans (203), whereas these compounds can be nitrated with sulfonitric mixtures.

Aromatic compounds are readily nitrated by means of these mixtures, but here again the ortho and para derivatives are not formed in the same ratio as are the products from sulfonitric mixtures (409).

#### 6. MIXTURES OF NITRIC ACID WITH PHOSPHORIC ACID AND PHOSPHORIC ANHYDRIDE

Phosphonitric mixtures are perhaps even more important than acetonitric mixtures for the nitration of polymeric carbohydrate materials when maximum nitration with a minimum of degradation is required.

Efforts of the early workers were directed towards the production of cellulose trinitrate. Krauz and Blechta (243) carried out a systematic study of the reaction of phosphonitric mixtures with cellulose. The maximum nitrogen content which they were able to introduce (using a nitric-phosphoric acid-phosphoric anhydride mixture) was thirteen percent. Husemann and Schulz (210) likewise were unable to produce a cellulose nitrate with a nitrogen content of more than 13.1%. By contrast, both Lenze and Rubens (258) and

Nicolas (299) reported that phosphonitric mixtures seemed at least as efficient as acetonitric mixtures for the production of high-nitrogen cellulose nitrates. The former authors prepared a cellulose nitrate containing 14.1% nitrogen. It has now been established that the composition of the phosphonitric mixture used exerts a very great influence on the level of nitration which may be obtained (38a, 49b, 397). Alexander and Mitchell made a very thorough study of these mixtures (5) and were able to find reaction conditions under which both reproducible and predictable results could be obtained. Since this time the mixture of Alexander and Mitchell has taken on the status of a standard to which much of the recent work on cellulose nitrate has been referred (32b, 36a, b, 38b, 121, 204, 271, 365d, 377a, 417a, b). The mixture of composition nitric acid : phosphoric acid : phosphoric anhydride :: 64 : 26 : 10 has recently been recommended for use as a tentative ACS Standard (292b). Further confirmation of the ease of obtaining variable degrees of nitration in a more-or-less predictable manner has also been obtained (32b, 212, 266, 342). Unfortunately, although highly substituted products have been prepared, it seems that it has not yet been possible to obtain a completely substituted cellulose by means of phosphonitric mixtures (32a, 379).

A further disadvantage in the use of phosphonitric mixtures is the possibility of the formation of mixed esters (102). It has now been established that such esters are produced and for this reason Harland (174) avoided the use of phosphonitric mixtures. On the other hand, Berl and Rueff (38a) and Bennett and Timell (32a) considered that the amount of phosphate introduced was entirely

negligible. Davis (103) found that cellulose nitrates, prepared by means of phosphonitric mixtures, contained an average of one phosphate group for every eight hundred glucose units. These products were very stable to both storage and fractionation.

Phosphonitric mixtures are frequently used to convert celluloses to their nitrate esters prior to studies of their chain length and chain length distribution. It is therefore of very great importance that knowledge of any degradative action of the phosphonitric mixtures should be available. Staudinger and Mohr (369) seem to have been the first to make a systematic study of this effect. It was found that little or no degradation occurred, a conclusion which has since been confirmed by many authors (38b, 102, 111, 174, 342, 352, 384b, 398). Bouchonnet, Trombe and Petitpas (49b) have suggested that the role of the phosphoric anhydride is to inhibit degradation, which occurred in mixtures containing only nitric and phosphoric acids. In spite of the large body of evidence to the contrary, Gralen (156), Golova and coworkers (154, 156) and Meyer (286a) are still of the opinion that no reaction involving the use of nitric acid is possible without accompanying degradation. Similarly, Bennett and Timell (32a) have suggested that only highly purified cellulose may be converted to the tri-nitrate stage without the occurrence of some degradation.

Phosphonitric mixtures have been used to prepare the nitrates of many simple carbohydrates in good yield (149, 309). Replacement of a tertiary hydrogen atom by a nitrate group has been reported to occur in substituted malonic esters treated with this reagent (234).

## 7. DINITROGEN PENTOXIDE

### (a) Solutions of Dinitrogen Pentoxide in Polar Solvents.-

Dinitrogen pentoxide in solution in polar solvents is in its ionic form (99) and should thus be a very powerful nitrating agent: That it is shown by the following evidence. Both cellulose (114, 338b, 387) and starch (387) have been nitrated by its use, to give a cellulose nitrate containing fourteen percent nitrogen and a starch nitrate with 13.85% nitrogen. Rogovin and Tikhonov (338b) have compared the reactions of nitric acid solutions of dinitrogen trioxide, tetroxide and pentoxide. Solutions of the latter oxide gave the greatest enhancement of nitrogen content of the resultant cellulose nitrates. The degree of substitution was greater than could be obtained by these authors with either phosphonitric or acetonitric mixtures. Further, of the three oxides studied, dinitrogen pentoxide caused the least disarrangement of the fibre structure. The effect of dinitrogen pentoxide in phosphonitric mixtures has been studied by Bennett and Timell (32a). The degree of nitration achieved with cellulose was only slightly higher than found for the phosphonitric mixtures alone, and seemed to be independent of the amount of dinitrogen pentoxide present. No degradation of the cellulose chain was brought about. Mixtures of nitric acid, phosphoric anhydride and dinitrogen pentoxide were not as effective as phosphonitric mixtures alone.

Mixtures of dinitrogen pentoxide and phosphoric anhydride in carbon tetrachloride have been used by Cooper and Ingold (92) to convert benzoic acid to m-nitrobenzoic acid in yields of eighty

percent of the theoretical. Aromatic compounds have been nitrated by solutions of dinitrogen pentoxide in acetic anhydride (322).

(b) Solutions of Dinitrogen Pentoxide in Inert Organic

Solvents.- The usual solvents for dinitrogen pentoxide are chloroform and carbon tetrachloride, in which solvents dinitrogen pentoxide exists in its covalent form (80, 99, 159). However, the mixtures are powerful nitrating agents, as shown by the speed with which they react and the high degrees of nitration attained.

The nitration of aromatic and other compounds with carbon tetrachloride solutions of dinitrogen pentoxide has been studied by Haines and Adkins (170). With benzene the reaction was almost quantitative, and could be controlled to yield either the mono- or dinitrobenzene. However, trinitrobenzene could be produced only in the presence of sulfuric acid. The nitration of bromobenzene was interesting in that only p-nitrobromobenzene was produced, the usual reagents giving a mixture of ortho and para derivatives. This was in contrast to toluene from which was obtained a mixture of nitrotoluenes. Picric acid was formed from phenol. The reaction with other compounds was not so satisfactory; benzoic acid could not be nitrated and heptane rapidly reacted to give products which decomposed on distillation. The reaction with olefins was negligible when all reagents had been thoroughly dried. This is in contrast to the results reported by Demjanoff (104) who claimed to have produced dinitrates by this reaction.

With aniline, dinitrogen pentoxide yielded a mixture of the nitric acid salt of the amine and the N-nitro compound (200, 313a).

With benzotrichloride (318a, 395) a mixture of products was obtained; mono- and dinitrobenzoic acids and some nitrobenzotrichloride. This is in contrast to the reaction of a phosphonitric mixture in carbon tetrachloride solution, where only a mixture of nitrobenzoic acids was obtained (368).

By far the greatest use of this mixture, however, has been in the preparation of nitrate derivatives of carbohydrates. Derivatives of galactose (15), glucose (30a) and aldonic acids (413) have been prepared thus, in good yield. Cellulose has been nitrated by mixtures of dinitrogen pentoxide in chloroform and carbon tetrachloride. Dalmon, Chedin and Brissaud (99) obtained a cellulose nitrate which analyzed for the trinitrate. However Jullander (227) was unable to obtain a product with more than fourteen percent nitrogen and, moreover, showed that the product had been degraded to a significant extent. Bennett and Timell (32a) also could not repeat the work of Dalmon, Chedin and Brissaud, the nitrogen content of their product, which was degraded, not exceeding fourteen percent. Recent work on cellulose has been reported by Caesar and his coworkers, who have nitrated cellulose (68a), and starch and dextrans (68a, 69). Nitration times as short as ten minutes were sufficient. No information as to degradation of the polymers is given.

Use of mixtures of dinitrogen pentoxide, carbon tetrachloride and sodium fluoride has recently been introduced. Sodium fluoride was added to the usual mixtures in order to remove the nitric acid of reaction from solution, through hydrogen bonding (68b). Solutions

of this composition have been used for the nitration of cellulose (68c), starch (70), dextrin (70, 162) and maltose (70). The maltose nitrate prepared had a nitrogen content of 15.5% which shows that the degree of substitution was high. The nitrogen content of maltose octanitrate is 15.9%. Mixtures of dinitrogen pentoxide and sodium fluoride in acetone solution have also been used. Pectin nitrates containing 9.5% nitrogen have been obtained by means of this reagent (353).

(c) Dinitrogen Pentoxide.-- Liquid dinitrogen pentoxide has been used as a nitrating agent to prepare N-nitroanilines (23). The desired products were formed in only small yield, the yields of the corresponding o- and p-nitroanilines being large. All other nitrations with dinitrogen pentoxide alone involve use of this reagent in the gaseous state. The earliest reported use of gaseous dinitrogen pentoxide as a nitrating agent is that of Giersbach (142b) who studied the nitration of benzene. It was later used by Gibson (142a) in his preparation of tartaric acid dinitrate. More recently dinitrogen pentoxide has been studied in its reactions with cellulose. Dalmon (98) has reported the preparation of cellulose trinitrate in 99.3% yield, and Urbanski and Janiszewski (387) obtained similar results for the reaction of dinitrogen pentoxide with starch as well as cellulose. No study of the degradative effect of gaseous dinitrogen pentoxide seems to have been made on these products. Vollmert (393) has recently studied the nitration of pectins (to give nitrates with 9.7 - 10% nitrogen), cellulose and starch. By determination of the viscosities of solutions of the pectin nitrates

which had been subjected to the action of dinitrogen pentoxide gas for periods varying from ten to ninety-six hours he showed that no degradation had occurred. This showed that polymer-analogous nitration can be achieved by the use of gaseous dinitrogen pentoxide.

The most recent report on the reaction of dinitrogen pentoxide with polymeric material is the X-ray study by Mathieu (27a, c) of the nitration of cellulose. The reaction was shown to be completed in twenty minutes, with production of cellulose trinitrate. Shorter reaction times resulted in products with lower nitrogen content. Hopes that the nitrogen contents of the products could be varied at will by variation of the reaction times were not realized (29). It was found that the products substituted to less than the theoretical extent were not uniform.

### C. THE CHEMISTRY OF WOOD

#### 1. THE COMPONENTS OF WOOD

Although the composition of wood varies widely from species to species, from tree to tree within the same species and even from one part of the same tree to another, most woods have a composition approximating the following: lignin, 25 - 30%; cellulose, 50%; hemicellulose, 15 - 25%; extractives, 1 - 10%, values of the former magnitude being the more common; minor amounts of ash, pectic and other material. As a beginning for this discussion, the following rough working definitions are given. Holocellulose is the total carbohydrate content of the wood, and is made up of both cellulose and hemicellulose. Cellulose is that part of the carbohydrate which

is composed of polymers formed from  $\beta$ -glucosidic units linked in the 1,4' positions. Hemicellulose is the non-glucose carbohydrate portion of wood. Lignin, in turn, is the non-carbohydrate fraction of wood. The extractives are not part of the mature cell wall, but exist in intercellular space. They are readily removed by treatment of wood with neutral organic solvents (hence their name) and are generally considered apart from the general chemistry of wood. Studies on wood itself are most often concerned with extractive-free samples.

## 2. THE STRUCTURE OF WOOD

It is only recently that reliable data on the position of the various components in the cell wall have become available. In mature wood, each cell is separated from its neighbours by a thin layer of "intercellular substance" termed the middle lamella. Approximately seventy percent of the material in the middle lamella is lignin (13, 17). The remaining thirty percent is thought to consist of hemicelluloses and perhaps minor amounts of pectic substances (17). The middle lamella is isotropic, i.e., it has the same properties in all directions. It has been suggested that the middle lamella may act as a type of adhesive to bind the cells together.

The anisotropic outer part of each cell proper is a thin layer, the primary wall. It is also highly lignified, but the relative content of carbohydrate material (cellulose and hemicellulose) is greater than in the middle lamella. There is evidence that the

primary wall is very important with respect to the chemical utilization of wood.

The secondary cell wall, which forms inside the primary wall and surrounds the lumen, appears only in maturing cells. It is relatively thick and consists almost entirely of cellulose although some lignin may also be present. Removal of the lignin by chemical means leaves a cellulose which can further be broken down into fine, threadlike structures (fibrils). The alignment of fibrils in the secondary wall is not uniform and three distinct layers can be detected. The planes of the separate layers are at an angle to each other, but all of the fibrils in each layer are parallel to each other. In the layers next the primary wall and the lumen, the fibrils lie at right angles to the longitudinal axis of the cell. The fibrils of the middle layer are aligned in a direction parallel to the long axis of the cell.

Meyer (286) has suggested that lignin, cellulose and hemi-cellulose are each arranged in separate layers which run through the fibre. Be that as it may, it is known that most methods for isolating the components of wood are fairly drastic (see section C-3) so that the isolated products do not always bear a strict relationship to the original material in situ. This is particularly true of lignin where the products isolated by different methods may vary considerably in composition. Because of this, it has become necessary to distinguish between the non-carbohydrate component as it occurs in the wood cells (now called protolignin) and the isolated component, for which the term lignin is reserved. This distinction

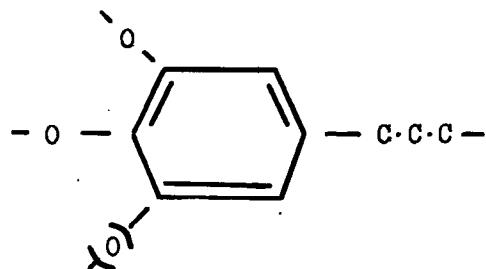
will be maintained during the rest of this discussion.

It is still not universally accepted that protolignin exists as such in wood. For instance Hilpert and his co-workers (51a, 168a, 197, 198) consider that the lignin isolated from wood (and other woody plants such as straw) by the usual methods, is formed from carbohydrate material during the isolation. Most experimental evidence, however, supports the theory of a preformed protolignin in mature and dead wood cells.

Little is known concerning the structure of either lignin or protolignin (51a, 175). Although the lignins (and presumably the protolignins also) isolated from different species vary somewhat in composition, it is generally considered that there is a common building unit--the phenylpropane nucleus. Protolignin is thus assumed to be aromatic in nature. It has been defined by Brauns (51a) as

"...that incrusting material of the plant which is built up mainly, if not entirely, of phenylpropane building stones; it carries the major part of the methoxyl content of the wood; it is unhydrolysable by acids, readily oxidizable, soluble in hot alkali and bisulfite, and readily condenses with phenols and thio compounds."

The manner of linkage of these simple units, both one with the other



and with the other components in the cell wall, is unknown. Because there is much evidence that the hemicelluloses of wood are very closely

associated with the protolignin (371), a short discussion of the structure of wood from the point of view of the protolignin - carbohydrate bond will be included here.

There are three main theories concerning the nature of the bonding of protolignin in the cell wall. According to the first of these, wood is considered to be a mechanical mixture of the various components. One of the more striking arguments for this theory is the fact that small amounts (2 - 3% of the weight of wood) may be extracted with ethanol (52), to give what is known as Brauns' native lignin. The very slight solubility is explained in two ways: (1) Although protolignin is present in the free state in wood, all molecules do not possess the same degree of polymerization, so that some of them are small enough to go into solution and others are not. (2) The intermeshing of highly polymeric substances is such that each prevents the others from "escaping" into the solvent (260a). Although some authors have claimed that larger amounts of protolignin may be extracted from wood which has been very finely ground (41) this evidence is much disputed, other authors (52) finding no such enhancement of solubility. An explanation for such discrepancies may lie in the results of some recent work on wood cellulose. It was found that cellulose was much degraded by fine grinding, indicating that chemical bonds may be broken by this means (288). Thus, the greater solubility of protolignin in more finely ground wood would indicate little concerning its actual bonding in the cell.

X-ray studies on wood cellulose in situ and on isolated cellulose

showed the same pattern (260a) indicating that the cellulose must have the same crystal structure in both instances. It was therefore concluded that cellulose cannot be chemically bound to any of the other constituents of wood. Furthermore, the X-ray diagram showed that the cellulose was more perfectly crystalline after the removal of protolignin, indicating that there had been no great disruption of bonds. This evidence, however, applies only to the cellulose component of wood, and not to the hemicellulose component.

Ultraviolet absorption spectra also seem to indicate that protolignin is not chemically bound, since the spectra of some lignins seem to be very similar to those attributed to the protolignin in whole wood (106).

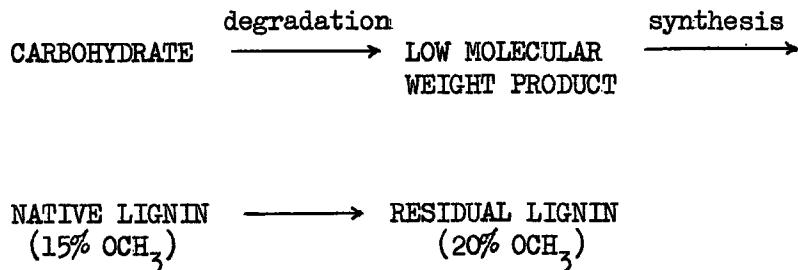
There is little chemical evidence to support the view that there is no chemical bonding of the components of wood, one with the other. All that seems certain is that not all of the cellulose can be bound to protolignin, since about half of the amount present can be removed by treatment of whole wood with solutions of cuprammonium hydroxide or cupriethylenediamine (198, 325). Some of the hemicellulose may be dissolved by treatment of the whole wood with dilute solutions of sodium hydroxide, but here again the amount removed is not the total present (371).

The effect of various organisms on wood has also provided some evidence to support the mechanical incrustation theory. For instance, after thorough extraction with ethanol to remove all soluble protolignin, finely ground wood was subjected to attack by cellulose-destroying fungi for several months (106, 356). After such treat-

ment, the residue was again extracted with alcohol which resulted in the solution of additional amounts of protolignin. However, although the amount of material extracted by alcohol after attack by the fungus was eight times that originally removed, the actual amounts were small (3.3% and 0.4%, respectively, indicating that only about one-eighth of the protolignin was removed).

Since the material extracted both before and after the attack by fungus had the same properties, it was considered that decomposition of the cellulose network had made it possible for the protolignin, no longer mechanically held, to go into solution. The similarity of the lignins isolated from several different species of woods also argued against the existence of a cellulose-protolignin bond.

It was further suggested that the following scheme (106) is possible, and shows that only the relatively non-polymerized protolignin can be removed by solvent action. Mention of this hypothesis



is made here, since it has been suggested that hemicellulose may be the intermediate between the first-formed pectin and the later-formed protolignin.

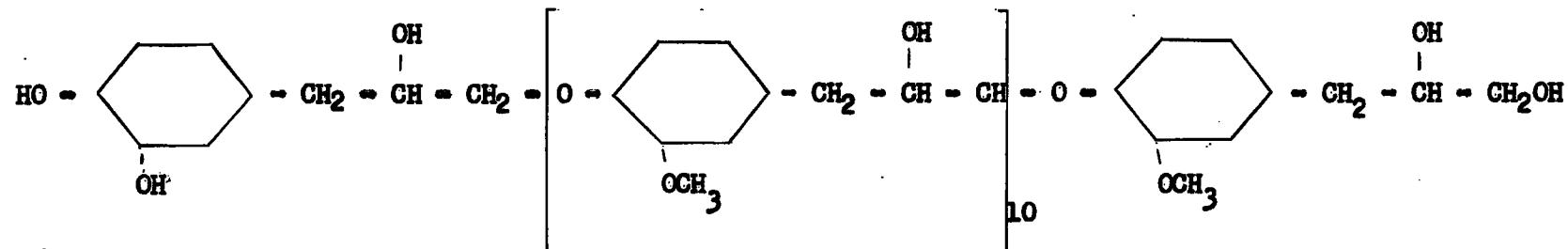
Although it is a quarter of a century since Freudenberg suggested a model for the cell on the basis of the mechanical incrustation theory (130), it still fits most of the facts as they are known.

The smallest morphological units of cellulose are the so-called micelles, which occur in the ribbon-shaped bundles of cellulose molecules. These micelles are joined together by the penetration of longer-than-average molecules from one micelle to the other, so that cellulose forms a complete network. In the spaces of this network, a three-dimensional protolignin network is gradually formed, so that its mesh is the negative of that of the cellulose. That which Freudenberg termed primary lignin was assumed to have been synthesized from carbohydrate material. Primary lignin was assumed to be an oligo-polymer of some twelve units (the formulae given by Freudenberg (Figure I) are no longer considered to be correct, but are given here merely as an illustration of the general theory of the mode of formation of lignin). Freudenberg's primary lignin may perhaps be identified with the native lignin of Brauns, and the material released from wood after it has been attacked by fungi.

Polymerization of the primary lignin to a three-dimensional network of irregularly sized polymers (the secondary lignin) was then postulated to occur. During this process, the cellulose would be completely enmeshed in the lignin network (corresponding to what is now termed protolignin), which was then filled with a "jelly" of pectic and pentosan materials. (Recent evidence would suggest that hexosans must be added to this list also.)

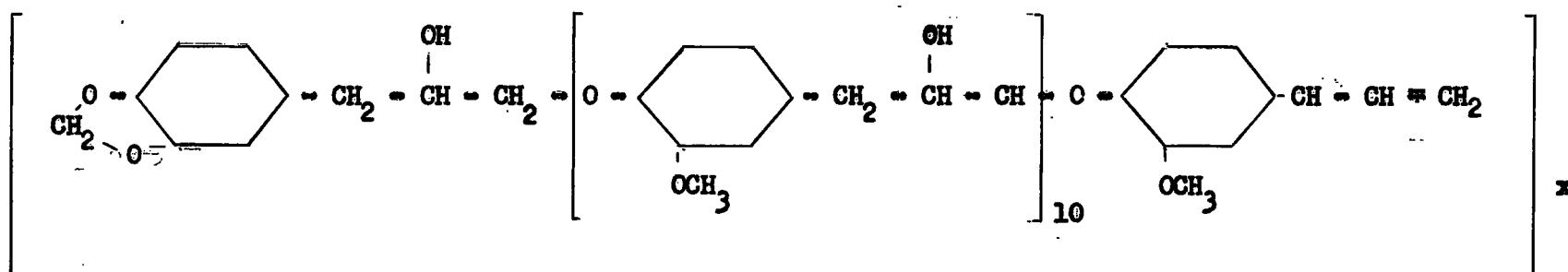
Freudenberg obtained some rather striking evidence for the validity of such a picture. Working with very thin slices of wood, the cellulose was carefully removed by gentle hydrolysis with dilute

FIGURE I  
Freudenberg's Formula for Lignin



primary lignin

36a



secondary lignin

acid, followed by extraction with cuprammonium hydroxide. Although the network had shrunk considerably, it still retained its original form, as shown by a microphotograph. The "holes" corresponded exactly to the positions of the cellulose fibres originally present. Freudenberg believed that behaviour such as this could be explained only on the basis that protolignin polymers are three-dimensional, that the cellulose is separately embedded in the protolignin network and that no chemical bonding exists. He compared this model to reinforced concrete, the cellulose being the iron network, and the hemicelluloses and protolignin the concrete.

Proponents of the theory that protolignin is chemically bonded to the carbohydrate fraction of wood have also found much evidence to favor their viewpoint. Among the most convincing is the extreme insolubility of wood, or any components thereof, in neutral solvents, including water. Separation of the various components can be achieved by use of basic, acidic or oxidizing reagents, but under rather drastic conditions (which will be discussed in the next section). The need for drastic conditions in order to effect separation, coupled with the fact that seldom is a clean separation effected, strongly suggests that chemical bonds are concerned. Furthermore, it is known that the isolated material is often more soluble than it was in situ, suggesting that hydrolysis preceded the original separation (405).

The presence of hemicellulose in the middle lamella, in close association with the protolignin also makes the presence of a chemical bond very likely.

The isolation of lignin-carbohydrate complexes has been reported by a number of authors. One of the earlier of such reports is that of Hagglund and Bjorkman (169) who, by treatment of sprucewood for a short time (30 - 40 min.) at a low temperature (10 - 15° C.) with concentrated hydrochloric acid isolated a residue which they thought was a usual hydrochloric acid lignin. However, on retreatment with concentrated hydrochloric acid, the residue was further degraded and considerable amounts of sugar were found in the hydrolyzate. Treatment with hot, dilute hydrochloric acid had a similar effect, both fermentable and non-fermentable sugars being present.

The behaviour of nitrated woods also gives evidence of the close association of protolignin with carbohydrate material. It has been noted in many instances that the solubility of nitrated wood and pulps in acetone varies directly with the degree of delignification of the starting material. Thus Mitchell (5, 292a), Timell (365a, b, c, 377b, e, 378) and others (61, 62, 118, 158, 193) have found that relatively complete solubility of the wood nitrated with phosphonitric mixtures is attained only after the reaction has been allowed to proceed for some time. It has been postulated (5, 377b, 392a) that during this long reaction time the protolignin is attacked in such a way that any bonds with carbohydrate material are broken. Similar behaviour has been noted in the nitration of pulps (1b, 5, 59a, 60a, b, 62, 74, 193, 221, 363, 365c, 377e). In three instances (1b, 61, 62) the claim of the actual isolation of a lignin-carbohydrate complex has been made.

Other lignin carbohydrate complexes have been isolated from poplar wood which had been treated with chlorine under anhydrous conditions (380, 381), from the acetic acid lignin of beechwood (232), and from enzyme-attacked wood (325). Evidence that hydrolysis of chemical bonds must precede the separation of components of wood has been found by Konkin and Rogovin (239b), Tachi and Yamamori (373), Traynard and his co-workers (381) and Lewis (260a). In all but a very few instances (1b, 62) it was the hemicellulose fraction of the carbohydrates present which was involved.

There is yet a third theory as to the nature of the binding of the components in wood--that the binding involves physical forces rather than the purely mechanical means postulated in the mechanical incrustation theory. Proof for the validity of such a theory is hard to attain. However, as pointed out by Ranby (332c), although the energy of one hydrogen bond is only of the order of two to ten kilocalories per mole, the total effect for a mixture of carbohydrate molecules each with two, three or four unsubstituted hydroxyl groups could be expected to be large. Support for such a theory has been obtained very recently by Snyder and Timell (365c). These authors described an experiment in which an artificial mixture of nitrated cellulose and nitrated mannan was denitrated, and then subject to extraction with 17.5% alkali, the usual reagent to achieve separation of cellulose and hemicellulose. However, in this case complete separation was not effected even after three such treatments.

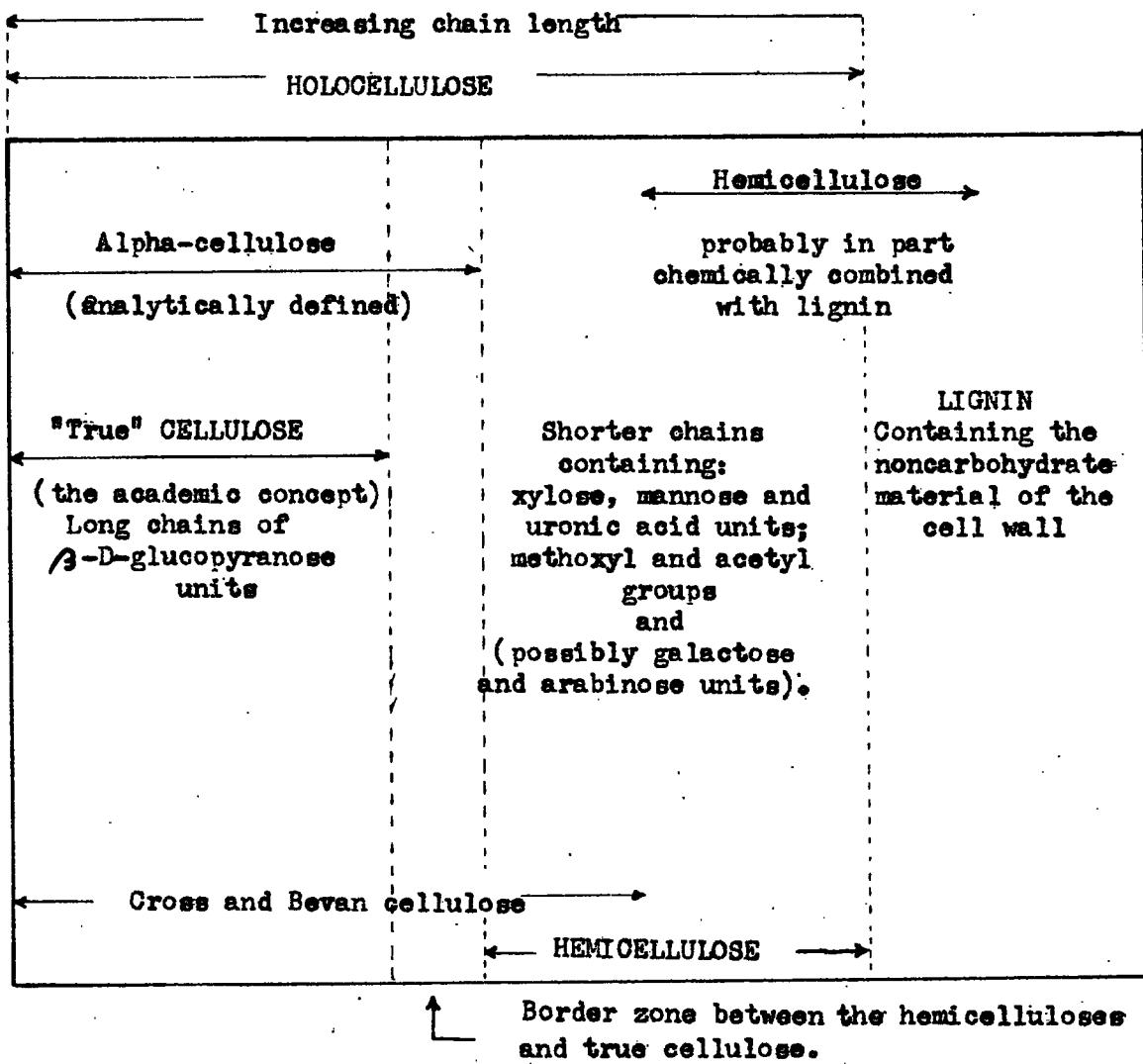
### 3. ISOLATION OF THE COMPONENTS OF WOOD

Available methods for separation of the components of wood most often involve treatment under conditions which may be termed drastic. In addition to leading to isolated products which may be altered chemically from their states in situ, these treatments generally result in the destruction of other components present (22). A further disadvantage arises from the fact that no known method is selective enough to effect a clean separation of the components. Furthermore, as can be seen by reference to Table III, the nature of the isolated product is very dependent on the method of isolation. Protolignin and the hemicelluloses are particularly affected so that the terms lignin and hemicellulose must be defined with reference to the manner in which the products were isolated. These difficulties in terminology have been illustrated by Wise and Ratliff (408) from whose paper Figure II is reproduced.

The above-mentioned difficulties are very pronounced in the case of the hemicellulose component of wood. Recently there has been much work on the fate of hemicelluloses during industrial and laboratory pulping processes. Comprehensive studies on the waste liquors have been carried out by Timell and Jahn (378), Harwood (176), Browning and Bublitz (58), Wise and his co-workers (407), McCarthy and Heritage (274), Lea (256), Boehn (46), Bjorkvist and co-workers (42), Shaw (360) and many others. Results obtained by all of these authors are in general agreement and show that "complete" delignification of wood cannot be brought about without very significant losses of carbohydrate material--glucose, mannose, xylose,

FIGURE II

COMPONENTS OF THE EXTRACTIVE-FREE CELL WALL  
From Wise and Ratliff (408).



Alpha cellulose "... is defined in analytical terms. It is the alkali-insoluble fibrous residue obtained under carefully controlled conditions from a mixture of polysaccharides, such as those found in wood pulps, "Cross and Bevan cellulose," or "holocellulose." Thus, it is largely "true" cellulose (with its long glucopyranose chains). However, it retains some mannose and/or xylose and uronic acid units as well."

"... true cellulose may be defined academically in terms of a homopolymer — i.e., the alkali-resistant glucose chains in wood. On the definition of our choice will depend just what is meant, not only by the term "cellulose," but also by the total hemicellulose content of a particular wood."

TABLE III  
Methods for the Isolation of the Components of Wood (a)

Component isolated	Starting Material	Reagent	Name of Isolated Component	Disadvantages (b)
Lignin	whole wood	organic acid	acetic acid lignin, etc.	C+
		alcohol/HCl	methanol lignin etc.	L-
		alkali	alkali lignin	I
		$\text{CuSO}_4/\text{H}_2\text{SO}_4$	cuproxam lignin (Freudenberg lignin)	L-
		HCl (conc.)	Willstatter lignin	C+
		$\text{H}_2\text{SO}_4$ (72%)	Klason lignin	L-
		alcohol	(Brauns') native lignin	L-
		$\text{HIO}_4$	(Purves') per-iodate lignin	L $\rightarrow$
		$\text{HNO}_3/\text{CH}_3\text{CO}_2\text{H}$	-	L $\rightarrow$
		acetic acid	-	L-
Pulp	whole wood	$\text{HNO}_3/\text{H}_3\text{PO}_4$	-	L $\rightarrow$ s
		$\text{NaHSO}_3$ (c)	-	L $\rightarrow$
		alkali or neutral and beating	semichemical pulp	L+
		$\text{NaHSO}_3$	sulfite pulp	C-
		$\text{Na}_2\text{S}/\text{NaOH}$	sulfate pulp	L+
		$\text{HNO}_3$	-	D.P.
		NaOH	soda pulp	C-
			-	C-
			-	L+

(a) General references: 168a, 406a.

(b) Disadvantages of the method used for isolating the component:  
 C+, hexosan is retained in the preparation; C-, loss of carbohydrate during isolation; L+, delignification is incomplete; L-, extraction of the lignin is incomplete; L $\rightarrow$ , the lignin has reacted chemically with the extraction medium; L $\rightarrow$ S, the lignin is isolated as a soluble derivative; D.P., the degree of polymerization of the cellulose is decreased; I, the preparation is not homogeneous.

(c) Ref. 67

TABLE III (contd.)

Holocellulose	whole wood	$\text{Cl}_2$ $\text{NaClO}_2/\text{H}^+$	-	C-
Hemicellulose	whole wood holocellulose whole wood	alkali alkali $\text{H}^+$	wood gum - -	L+ C- C- C-

arabinose, galactose and uronic acid. Furthermore, the celluloses obtained by extraction of the various pulp and holocellulose preparations are now known to contain carbohydrate residues other than glucose (4, 326, 415).

This gives rise to two further difficulties, one of which concerns the identity of wood and cotton celluloses (1a, 40, 406a). While it is generally agreed that in wood cellulose there are long chains of  $\beta$ -glucosidic units linked in the 1-4' positions, it is possible that mixed chains may also be present. This would be in contrast to cotton cellulose in which glucose residues are the only units. On the other hand, recent work (365c) has shown that artificial mixtures of mannan and cellulose can not be completely separated by the usual extraction methods. This suggests that much of the non-glucose carbohydrate found in wood celluloses is merely adsorbed on the surface and is not chemically bound. The work of Yllner and Enstrom (415) on the adsorption of xylan on cellulose points in the same direction.

A second difficulty, arising naturally from the first, concerns the definition of hemicellulose (371, 405). The portion of

the wood carbohydrates which is not mainly glucosidic and which can be extracted from wood readily by treatment with dilute acid or alkali was given the name hemicellulose by Schulze. He and others have further suggested that polymers isolated from these extracts be named according to the carbohydrates found in greatest quantity in the hydrolyzates, e.g., mannan, xylan, arabogalactan, etc. However, since it has often been shown (89, 199, 224) that preparation of "pure" polymers is very difficult, this method of nomenclature may not be entirely accurate. Moreover, since the existence of units other than glucose as integral parts of the cellulose chain and of glucose units in the so-called hemicelluloses has been neither proved nor disproved (332a), the term hemicellulose itself may not be meaningful. The term polyose has been proposed in its place. Yet another classification is based on the component of wood with which the particular carbohydrate fraction is most closely associated. This gives rise to the terms cellulosans--those polymers which appear to be difficultly separable from cellulose--and the polyuronides which contain uronic acid units and are seemingly very closely associated with protolignin. This is clearly illustrated in Figure II.

Another classification is based on the method of preparation from the alkaline extract of wood. The fraction readily precipitable by addition of acid was termed Hemicellulose A, that from addition of alcohol to the acidified solution, Hemicellulose B. However, it seems that universal agreement as to nomenclature has not yet been attained, so that all methods of classification are found in the literature.

The chemistry of the hemicelluloses has been reviewed recently by several authors (199, 224, 326, 371, 405). Typical results of the work are shown in Table IV. In general, relatively large amounts of D-xylose, D-mannose and D-glucose are found in the hemicellulose fractions of most woods. L-Arabinose, D-galactose and L-rhamnose are present in smaller amounts. Uronic acids are also present in most, if not all, woods. Mannose occurs to a greater extent and xylose to a lesser extent in softwoods than in hardwoods. Softwoods also contain more galactan than hardwoods. Xylose seems to form the "backbone" of many polymers, while the other sugar residues and uronic acids are often present as side chains.

#### 4. THE CHEMISTRY OF WESTERN RED CEDAR WOOD

The chemistry of western red cedar (Thuja plicata) has been little studied. Analyses of the bark (95), the extractives (26) and a study of the properties of western red cedar butt rot (280) have been reported. Studies on the pulping properties of western red cedar have also been carried out (57, 205), but none of this information is of interest for the purposes of this discussion.

Analyses of western red cedar, by the usual standard methods, have been carried out by both Wise and Ratliff (408) and Lewis (260b). The results are summarized in Table V. Anderson (7) was the first to isolate a small amount of pectic material (0.11%) from mature western red cedar and from the holocellulose prepared from this wood. The presence of small amounts of free L-arabinose

TABLE IV  
The Hemicelluloses of Wood

Wood	Hemicellulose*	Carbohydrate Present **	Reference
Aspen	xylan	gl, ga, a, r, m, u.a.	224, 331
Oak	-	x, u.a., gl.	405
Black locust	-	x, u.a., gl.	405
Lemon wood	-	x, u.a., gl.	405
White birch	-	x, u.a., gl, m.	377e, 405
Cotton wood	-	x, u.a., gl.	405
Box wood	-	x, u.a.	371
Eucalyptus	-	x, u.a.	371
Sugar maple	-	x, u.a.	406b
Beech	xylan	r, u.a.	199
Black spruce	-	m, a, x, gl, ga.	89
Larch	arabogalactan	-	199
White pine	-	x, u.a., m, gl.	405
Slash pine	-	m.	10, 225, 405
White spruce	-	m, x.	377b
Balsam fir	-	m, x, a, ga, u.a., gl.	365b
Loblolly pine		x, gl, m, a.	22

\* An entry in this column indicates that a reasonably pure polymer has been isolated.

\*\* a = arabinose; gl = glucose; ga = galactose; m = mannose;  
r = rhamnose; u.a. = uronic acid; x = xylose.

TABLE V  
Analysis of Western Red Cedar

Determination	Content of Wood (%) *	
	Ref. 408	Ref. 260b
Ash	0.27	0.24
Acetyl	0.53	0.53
Lignin	32.5	32.6
$\alpha$ -cellulose	52.7	52.8
$\alpha$ -cellulose (corrected)	47.5	-
Hemicellulose	14.65	-
Hemicellulose A		10.2
Hemicellulose B		4.5
Xylan	8.1	8.1
Uronic anhydride	4.2	4.2
Mannan	5.1	5.1
Pentosan	-	10.3
Extractives	-	10.2
Tannin		1.5
Pectic acid		0.11
Methoxyl		5.58
Methoxyl in lignin		15.6
Nitrogen		0.11
Residues associated with $\alpha$ -cellulose**		
Uronic acid		1.3
Uronic anhydride		2.4
Pentosan		1.7
Xylan		1.5
Mannan		6 - 7

\* All values except those for extractives, pectic acid and tannin are calculated on a moisture-free extractive-free basis.

\*\* Calculated on the basis of the isolated cellulose.

(0.27% isolated) in western red cedar heartwood has been demonstrated by Anderson and Erdtman (8). In comparison with four other softwoods on which analysis was carried out—western hemlock, loblolly pine, Douglas fir and eastern spruce—western red cedar wood is very high in extractives and has a fairly high lignin content. Its content of  $\alpha$ -cellulose is the lowest of the woods analyzed (260b). The acetyl content is also low.

The characteristics of an unbleached kraft (sulfate) pulp from western red cedar have been studied (261). Results of analysis of the pulp are shown in Table VI. In comparison with the kraft pulps from the same four woods as mentioned above, that from western red cedar is low in both mannan and uronic anhydride but fairly high in the content of xylan. This pulp was nitrated by means of a phosphonitric mixture (195). The yield of nitrated material was 171%, which was almost the same as that for the other pulps studied. The nitrates were fractionated by treatment with an ethanol-ethyl acetate mixture. Degrees of polymerization of the fractions were determined. The average degree of polymerization for western red cedar kraft pulp was rather higher than that of the other pulps. The distribution of short, medium and long chain material is shown in Table VII. The amounts of medium and short chain material are relatively low, the amount of long chain material is relatively high.

A study of the orientation of cellulose chains in the kraft pulp fibres from western red cedar was also carried out (47a, b). Of the woods studied, western red cedar was intermediate in order

TABLE VI

Analysis of an Unbleached Kraft Pulp from  
Western Red Cedar (261)

Determination	Content of wood (%)
$\alpha$ -cellulose	85.4
$\alpha$ -cellulose (corrected)	78.7
Hemicellulose A	3.7
Hemicellulose B	3.2
Mannan	22.8
Xylan	7.3
Uronic anhydride	1.5
Lignin	6.2
Ash	0.6
Extractives	0.8
Pectins	negligible

TABLE VII

The Distribution of Degrees of Polymerization in Western Red Cedar Kraft Pulp, Compared with Other Pulps (195)

Wood	Short-chain % D.P.	Medium-Chain % D.P.	Long-Chain % D.P.
Western hemlock	16 200	8 -	76 1560-1930
Western red cedar	10 130	7 -	83 1510-1946
Loblolly pine	10 96	9 -	81 1542-2091
Douglas fir	13 121	5 -	82 1604-2240
Eastern spruce	15.5 116	7.5 -	77 1546-2206
Western red cedar	10.13 130	3.16 765 3.30 1238	22.80 1510-1742 60.61 1881-1996

of preferred orientation. A higher degree of preferred orientation is associated with a lower ability to swell. Therefore it would seem that the swelling properties of western red cedar should be reasonably good and thus reaction of the carbohydrate portion of the wood should not be inhibited by this factor.

Fibre dimensions of the unbleached kraft pulp from western red cedar wood have been measured (155). The results are shown in Table VIII.

Very recently, the production of a satisfactory nitric acid pulp from western red cedar wood has been accomplished. Analytical data for this pulp are shown in Table IX.

## 5. TOPOCHEMICAL REACTIONS

(a) The Fine Structure of Cellulose\*.- Although much is known about the manner of linkage of glucose units and the arrangement of these in the unit cell of cellulose, these details need not be considered here. What is of concern is the arrangement of these long chains of 1,4'- $\beta$ ,D-glucosidic units in the fibre, i.e., the submicroscopic structure.

The number of units per chain varies with the source of the cellulose, those of cotton and ramie celluloses being the longest. While it is difficult to get an accurate estimate of the chain length of wood celluloses, recent work by Timell and others has shown that degrees of polymerization may be higher than at first

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\* General references for this section: 168, 288, 324, 406a.

TABLE VIII

Fibre Dimensions of Unbleached Kraft Pulp from  
Western Red Cedar (155)

Fibre length (mm.)	
arithmetic average	2.05
weighted average	2.76
Fibre width (mm.)	0.040
Area (sq. mm.)	0.089
Fibres per gram (million)	4.5

TABLE IX

Analysis of a Nitric Acid Pulp from Western  
Red Cedar (44)

Determination	Content (%)
$\alpha$ -Cellulose	90.1
$\beta$ -Cellulose	2
$\gamma$ -Cellulose	4.2
Extract (alcohol/benzene)	0.10
Sol. in 7.14% NaOH	9.6

thought. The separate chains of glucose anhydride units are held together in bundles (filaments, micelle strings, fibrils) of perhaps as many as a hundred. Diameters of the fibrils may vary from 50 - 100 Å, fibrils of wood cellulose being among the thinnest known (70 - 80 Å) (332a). Within the fibrils the chains are held together by secondary valence forces, such as hydrogen bonds or van der Waal's forces. Whatever the type of bonding, the arrangement of the separate chains is very important in determining the reactions which cellulose may undergo. The Fringe Micellar Theory, which is the one most widely accepted at present, postulates that the chains are parallel to each other only in certain regions. In other regions the arrangement is much more disorganized so that chains may cross, there may be larger spaces between them, etc. Thus, along the longitudinal axis of the fibril there are alternate regions of order and disorder. These are called, respectively, micelles or crystallites (this latter term being preferred) and the amorphous regions. The crystallites have a diameter of approximately 50 Å, a length of 400 - 600 Å<sup>c</sup> and an interspatial distance of 10 - 100 Å. There is no sharp boundary between the crystallites and the amorphous regions. Since the length of a single chain is in the range of 4000 - 12000 Å, one chain may span the amorphous regions between and take part in the formation of several crystallites. This is in contrast to the fibrils, between which there are no such connections.

In wood pulp the ratio of the amount of crystalline material to the amount of amorphous material is smaller than in cotton and

ramie celluloses. However, the degree of order in the crystallites of both wood and cotton celluloses is sufficient to produce characteristic X-ray patterns. It is assumed that secondary valence forces are acting to good effect in the crystalline regions but that there is little such linkage in the amorphous regions.

Cellulose fibres in turn are made up of bundles of fibrils held parallel to one another by hydrogen bonds or van der Waal's forces. Ultrasonic irradiation of cellulose can, in certain cases, effect disintegration of the fibres to fibrils. It should be mentioned that, although these fibrils seem to exist as such in the cell wall of wood, their presence in cotton and similar celluloses is questionable. It is possible that they could be formed in such celluloses during chemical or other treatment.

(b) The Mechanism of Reaction of Cellulose\*.- Since the very great majority of reactions of cellulose involve this substance in its solid state, the fine structure is an important factor in determining the nature of the products and the mechanisms by which they are formed. The amorphous and crystalline regions represent areas in which, respectively, reaction can occur rapidly, or reaction may be almost completely inhibited. Reactions which occur almost exclusively in the amorphous areas are termed intermicellar or microscopically heterogeneous. Those which occur throughout the whole fibre are termed intramicellar or microscopically homogenous.

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\* General references for this section: 168a, 187, 286, 288, 406a.

The power of a reacting substance to cause swelling, i.e., to force apart the cellulose chains and thus increase the distance between hydroxyl groups, determines, almost completely, the course of the reaction. Reagents which bring about swelling cause all regions of the fibre to be accessible for reaction, so that random substitution may occur and a uniform product result. It is now considered that reactions which occur after cellulose has been pre-treated in such a manner as to cause swelling, or in reagents which cause swelling, are intramicellar reactions. The first action to occur is the penetration of the reagent into the fibre. For some time, there have been two theories as to the exact mode of reaction of the swollen fibre. The first postulates that the amorphous regions, the surface of the crystallites and the surface of fissures in the crystallites react quickly with complete substitution of all hydroxyl groups. Only after this initial rapid reaction are the crystallites attacked. Thereafter, the reaction goes forward through the crystallites, layer by layer, until the centre of the fibre is reached. Thus, it is seen that, although the final product may be homogeneous (i.e., random substitution has occurred), products isolated before completion of reaction or before attainment of equilibrium would not be homogeneous (i.e., substitution had occurred preferentially in certain regions).

The second theory postulates that, although the more accessible amorphous and surface areas may be more rapidly attacked, reaction occurs simultaneously through the whole fibre. Thus, at all times during the reaction the product is homogeneous since random substitution

is occurring everywhere in the fibre. Such reactions are termed permutoid. It is now considered that most reactions which are accompanied by swelling are permutoid in nature. One important characteristic of these reactions is the preservation of crystallinity in the crystallites, so that the products of reaction show characteristic X-ray patterns which may, or may not, differ from that of the original cellulose.

Reactions which are not preceded by swelling of the fibres are termed intermicellar, microscopically heterogeneous or macro-heterogeneous. Here, reaction must start on the surface of the fibre and proceed inwards, layer by layer, i.e., attack is completely from the outside. Two reactions of this type are sometimes distinguished. Where the primary cell wall is only partially swelled and the secondary wall is penetrable, reaction starts only in certain areas of the surface, hence the name topochemical reactions. When the primary wall is completely swelled and the secondary wall is not penetrable, the reaction begins over the whole surface of the fibre and then is carried inward, layer by layer. Such reactions are termed typical heterogeneous.

Products of these reactions are heterogeneous, i.e. substitution has occurred only in definite regions of the fibre. The crystallites may be totally untouched except on the surface. Amorphous regions are, of course, attacked more readily. Thus, reaction may occur more readily across the fibre, rather than along it.

It is now recognized that all these types of reaction may occur, depending upon the experimental conditions and the reactant. Also,

the reaction may change in character during its course. For example, the initial stages of permutoid reactions may be heterogeneous due to the more ready reactivity of the surface and amorphous regions, but the reaction soon becomes homogeneous as attack commences in the crystalline areas also.

While it is now considered that the nitration of cellulose with sulfonitric mixtures is a permutoid reaction (133, 272b, 288), there is evidence that the products are not entirely homogeneous. Happey (173) claims to have found regions in cellulose nitrate where both the di- and trinitrate occur together. Miller and Timell (290) have recently found that cellulose nitrate was substituted to a greater extent in the interior, than on the surface, of the fibre when phosphonitric mixtures were used as nitrating agents. Mathieu (272b, c) has shown that the reaction of cellulose with gaseous dinitrogen pentoxide is permutoid in nature.

(c) The Fine Structure of Wood.— Some details of the fine structure of wood cells are known. It has already been mentioned that the fibrils of wood cellulose, which are among the thinnest known, seem to exist as distinct entities in the cell wall. This is shown by the relative ease of disintegration of wood cellulose to fibrils, when subjected to irradiation by ultrasonic vibrations (332b). It has further been suggested (332c) that hemicellulosic material absorbed on the surface of the fibrils acts as an "adhesive" holding them together. Ranby (332a), who has suggested that both polyuronides and waxes are closely related to the fibrils, has carried out some very interesting studies on the morphological

character of spruce holocellulose and hemicellulose. Spruce holocellulose was subjected to irradiation with ultrasonic vibrations. Electronmicrographs of the disintegrated material showed the fibrils as filaments embedded in a disperse phase which had no structure elements and which was probably hemicellulose. A similar examination of spruce hemicellulose showed the presence of a disperse phase only.

Ranby (332a) further examined the structures of  $\alpha$ -,  $\beta$ - and  $\gamma$ -celluloses\* as revealed in electronmicrographs. Only one structural unit was present in  $\alpha$ -cellulose—aggregates of fibrils, with only a very few free fibrils. This indicated the resistance of purified cellulose (i.e., cellulose which had been freed from hemicelluloses) to disintegration by mechanical agitation.  $\beta$ -Cellulose proved to consist of well-defined, thin, curved strings and small particles. The identity of the X-ray diagram for  $\alpha$ - and  $\beta$ -cellulose showed that the latter consisted only of disordered and broken fibrils. Neither fibrils nor distinct particles were seen in electronmicrographs of the  $\gamma$ -cellulose. Ranby therefore suggested that the  $\gamma$ -cellulose fraction was made up of wood polyoses and an "amorphous interfibriller substance of pulp."

There remains now to record the few known facts which may throw some light on the topochemistry of the nitration of wood. As with cellulose, ease of penetration of reagents into the wood structure

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\*  $\alpha$ -Cellulose is defined as the residue left after a wood pulp has been treated with strong lye.  $\beta$ -Cellulose is the material readily precipitated from the alkaline liquor by addition of acid. The carbohydrate material remaining in the acidified solution is termed  $\gamma$ -cellulose.

governs the character of the reaction (372). Wood, cellulose and lignin all have the same sorptive powers for water (406b). It has also been found, for beech and aspenwood (372) that the sapwood is much more readily penetrated by a pulping liquor than is the heartwood. In addition to being dependent upon the species of wood, there was also a variation in the amount of penetration in the same log and even within the periodic rings of beechwood. The variation in reactions of sap- and heartwood was found to be connected with the presence of tyloses\* in deciduous trees.

The swelling capacity of wood cellulose, as compared to cotton cellulose, is determined by yet another factor. It is known that, in cotton and other natural celluloses, the fibrils are oriented at only a small angle to the longitudinal axis of the fibre. In the secondary layer of wood cellulose, as has already been described, there are three layers of fibrils, two of which are oriented almost at right angles to the fibre direction. This arrangement offers resistance to swelling and may force some of the dimension change to occur internally, into the fibre cavity. Finally, it has been found that the ratio of the amount of amorphous and crystalline material is larger in wood pulp than in cotton linters (87a). Presumably this would also apply to the cellulose in situ, so that, in this respect, wood cellulose may be able to react more readily than cotton cellulose.

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\* Tyloses are growths of lignin and carbohydrate material in the vessel cavities of deciduous woods.

D. THE NITRATION OF ISOLATED COMPONENTS OF WOOD  
AND OTHER PLANTS

1. THE NITRATION OF LIGNIN \*

Results of the treatment of lignin with dilute nitric acid have been reported by a number of workers (review papers 51b, 112, 319). The main reaction seems to be one of oxidation since products such as oxalic acid (85, 125, 139, 207, 347) and acetic acid (347) have been isolated from the solutions. However, some nitration also occurs since nitrophenols (85, 125, 139, 386) have also been found as reaction products and nitrogen contents of 4.87 - 6.21% (347) have been found in the isolated lignins. A very recent report (307) concerns the treatment of a pine lignin with three percent aqueous nitric acid. The product of the reaction was reduced with Raney nickel and then treated with nitrous acid. Seemingly, diazotization occurred since an iodo compound could be prepared (by addition of potassium iodide) and a pink dye was produced in the coupling reaction with J acid.

More concentrated nitric acid results in loss of methoxyl (347) and dinitroquaiacol has been isolated as a product of the reaction.

Concentrated and fuming nitric acid also cause oxidation and nitration (194, 229, 347), as does treatment with sulfonitric mixtures (327). Such results show that little useful information regarding the structure of either lignins or protolignins can be obtained by studies conducted on the products of reaction with

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\* For the purposes of this discussion, lignin is defined as the non-carbohydrate material isolated from wood by one of the standard methods, as discussed in section C-3.

nitric acid. They also indicate the ease with which lignin is both oxidized and nitrated.

Kruger (245) isolated lignins from various plant seed hulls. They were nitrated with nitric acid and the products were isolated by precipitation from the reaction mixture on addition of water. From the results shown in Table X, it is seen that demethylation occurred to a rather large extent. Other lignins have been nitrated with nitric acid (197) and also with sulfonitric mixtures (263). In all cases the greater part of the nitrogen was introduced as the nitrate. Results are shown in Table X.

Nitrogen dioxide has been found to react quite readily with lignin (351). However, the formation of both carbon dioxide and oxalic acid showed that the reaction was accompanied by oxidation. Freudenberg and Durr (131) likewise studied the reaction of nitrogen dioxide on anhydrous lignin under carefully controlled conditions. The reaction seemed to go through two distinct stages, the uptake of nitrogen dioxide being followed by evolution of a gas (oxides of nitrogen) which was indicative of an oxidation reaction. Treatment of a methylated lignin with nitrogen dioxide resulted in the uptake of approximately four percent of nitrogen. There was loss of methoxyl groups (original methoxyl content, 28%; methoxyl content of the nitrated product, 23.5%) which appeared as methyl alcohol.

Freudenberg and coworkers (132) attempted to lessen the degree of oxidation during nitration by first acetylating a spruce lignin and then subjecting it to the nitrating action of a solution of dinitrogen pentoxide in chloroform, at -20° C. Although the acetyl

TABLE X  
The Nitration of Lignin from Various Sources

Source of Lignin	Methoxyl in Starting Material (%)	Yield of Nitrated Lignin (%)	Methoxyl in Nitrated Lignin (%)	Nitrogen Content of Nitrated Lignin (%)		Ref.
				Total	Ester	
Chestnut	0.5	trace	-	-	-	245
Hazelnut	5.8	4.6	2.2	6.2	-	245
Beechnut	9.0	5.2	3.1	7.4	1.5	245
Plum stone	17.0	15.3	4.8	5.8	1.6	245
Spruce	15	54	-	4.6	1.3	197
Spruce						
Methanol Extract of Nitrated Wood	-	-	-	6.9 - 9.8	3.9 - 5.8	263
Freudenberg	-	34-120*	-	2.4 - 9.3	0.2 - 5.6	263
Willstatter	-	101-126*	-	8.2 - 9.9	2.4 - 5.6	263
Tornesch	-	5.8-9.7	-	6.9 - 7.9	2.6 - 2.9	263

\* The yield varied with the acid mixture used for the nitration.

content remained constant, the methoxyl content dropped by thirty-three percent.

Lignosulfonic acids have been nitrated by Konig (238) and by Carpenter and Benson (73). Phenolic products were formed by treatment of the sulfonic acid with nitrous acid, a fact which suggests that lignin is at least partially aromatic in nature (238).

However, when the object of nitration is to study the structure of lignin, nitration by means of acetonitric mixtures seems to be the preferred method. Such a mixture has been used to prepare a nitrolignin on which studies of the sulfonation reaction were to be carried out (135). Hibbert and Marion (196) have studied the reactions of a glycol lignin when treated with a mixture of fuming nitric acid and acetic anhydride at -12° C. The product, which had been acetylated as well as nitrated, contained 8.48% methoxyl, 8.65% total nitrogen, 3.18% nitrate nitrogen and 2.57% nitro- and nitrosonitrogen. Retreatment of the nitrated lignin with a second batch of the nitrating mixture for five hours at 80° C. resulted in the lowering of the content of carbon but not of methoxyl.

Nitrogen was still present in the same forms as mentioned above. Some oxidation occurred during this treatment, as evidenced by the formation of brown vapors of oxides of nitrogen. Repeated treatments with the nitrating mixture at -12° and 80° C. resulted in a very slight lowering of the methoxyl content.

Ali and Khundkar (6) have treated lignins isolated from rice husks, betel nut husks and bamboo with acetonitric mixtures. In all cases the nitrogen-containing groups introduced were found in

the aromatic ring rather than on the aliphatic side chains of the product.

Friese and Ludecke (137) have prepared and nitrated a number of lignins, using a mixture of nitric and acetic acids. Although nitrogen contents of up to 8.5% were attained, in no case was it possible to inhibit decomposition completely, as evidenced by evolution of oxides of nitrogen. Drastic reduction in methoxyl content also occurred (from 15% to 3.7 - 4%). The weight ratio (i.e., the ratio of the weight of the product to the weight of lignin used in the reaction) was 0.80 for Tornesch lignin. When acetic anhydride was added to the nitrating mixture, the ratio was 1.01, and the nitrogen content 8.52%, of which 6.45% was present as the ester. The methoxyl content was 5.99%. A mixture of nitric and phosphoric acids gave results similar to these.

## 2. THE NITRATION OF HOLOCCELLULOSE AND PULPS

Using the nitration technic as a tool, Bryde and his coworkers have carried out extensive studies on pulps prepared by several different processes. Both sulfite and semichemical\* pulps were examined by Bryde and Smith (62). Nitration was carried out by means of the phosphonitric reagent of Davidson (102). The nitration liquor was used in hundred-fold excess (by weight) and the reaction was allowed to proceed for four hours at 0° C. After

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\* Semicchemical pulps are those prepared by both chemical and mechanical treatment of wood (168). Pulps from various processes often have quite different compositions, i.e., an acid pulping liquor gives a pulp low in lignin but high in hemicellulose content, whereas with an alkaline liquor, the converse is true.

thorough washing with fifty percent aqueous acetic acid and then with water, the nitrated product was extracted with cold methanol for one to two days, the length of time depending upon the degree of delignification of the original pulp. The residue from the methanol extraction was, in turn, extracted with acetone. From these treatments, three fractions were separated; a methanol-soluble fraction, an acetone-soluble fraction and a residue which was insoluble in both methanol and acetone. It was found that the amount of residue varied inversely as the degree of delignification of the pulp. Highly lignified pulps were but little soluble in acetone, whereas delignified pulps were almost completely soluble in this solvent. Both cellulose nitrate and nitrated lignin were present in the residue, and Bryde and Smith suggested that a chemically-linked lignin-carbohydrate complex had been isolated. It was further determined, from viscosity data, that only the most highly polymerized part of the cellulose was found in the residue. This cellulose presumably had been bound to the protolignin in situ. Since residues were isolated only from pulps which were still highly lignified, it was considered that the protolignin-carbohydrate linkage was cleaved during the early part of the pulping cook. Similar residues have been isolated from pulps by Abadie (1b).

A very similar study was carried out by Bryde, Ellefsen and Smith (60b), using paper and rayon grade pulp. Here, the methanol-soluble fraction was so small that it was not considered necessary to isolate it. As found previously, the acetone-insoluble fraction appeared only in samples high in lignin, such as some hardwood pulps.

Abadie (1b) has applied the method of Bryde and Smith (62) to

the study of sulfite and other acid pulps from fir wood. The methanol-soluble fraction was shown to be nitrated lignin and the insoluble residue, corresponding to that of Bryde and Smith, seemed to be combined lignin and carbohydrate nitrates. The acetone-soluble fraction was carbohydrate in nature and was subdivided into a fraction which would not precipitate from solution on addition of water, and a fraction which did precipitate on addition of water. The former fraction was shown to contain xylan and other carbohydrate polymers of low molecular weight, while the latter was subsequently shown to be  $\alpha$ -cellulose (3). Abadie (1b) also confirmed the observation that the carbohydrate which was so closely associated with lignin had an extremely high degree of polymerization.

Attempts to obtain pure cellulose from pulps through fractionation of their nitrate derivatives have been reported by Dymling, Giertz and Ranby (115). Their starting material (ramie pulp, and various pulps from spruce, pine and straw) was treated with a phosphonitric mixture at -10° C. A solvent - nonsolvent system of ethyl acetate and ethanol was used to separate the nitrated products into several fractions. The soluble fractions of all wood pulps contained large amounts of glucose, mannose and xylose. The residues contained glucose with smaller amounts of xylose and mannose. Straw pulp showed much xylose in the residue (28%). The authors estimated that one-third of the soluble fraction of all nitrated pulps was glucose and that this glucose did not belong to the resistant cellulose framework.

Nitration technics have also been used in the study of the

polydispersity of cellulose in wood pulps. From highly purified pulps (i.e., pulps containing little lignin), Herrent and Govaerts (188) prepared the nitrate derivatives by use of a phosphonitric mixture. Methanol extraction of the product removed only a small amount of material which was thought to be short chain carbohydrate molecules. The remainder of the nitrated material was soluble in acetone.

Nitration of pulps on an industrial scale, by means of sulfo-nitric mixtures has been reported by Schur and McMurtrie, (358), Schur and Hoos (357) and Jahn and Coppick (218b). Further work involving nitration of pulps has been reported by Ellefsen (116), Bryde (59a, b, 60a, 61), Alexander and Mitchell (5), Heuser and Jorgensen (193), Centola (74), Sihtola and Aejmalaeus (363), Snyder and Timell (365c), Timell (377e) and Jensen and Rainio (221). There is general agreement on the solubilities of the nitrated pulps with respect to their degrees of delignification.

Nitration of holocelluloses has been reported by several authors. Harwood (176) nitrated holocelluloses, prepared by different treatments of whole wood with acidic sodium chlorite solutions, in an attempt to follow the loss of carbohydrate material during the delignification process. After nitration with a phosphonitric mixture, the products were thoroughly washed and stabilized by extraction with methanol. The residue was then treated with acetone, in the ratio of two hundred and fifty millilitres of acetone per gram of nitrate. Nitrated holocelluloses from all preparations gave fractions insoluble in this volume of

acetone. The acetone-soluble material could be fractionated by addition of water to the acetone solution. The fractions readily precipitated by this treatment were white, fibrous solids while the more soluble fractions proved, on recovery, to be white, electrostatic powders. These latter were shown to be nitrates of hemicelluloses and cellobextrans (short-chain celluloses). Eguchi (120) also has reported the separation of hemicellulose and cellulose nitrates by precipitation from acetone solution.

The characteristics and compositions of a number of nitrated holocelluloses from paper birch wood have been studied by Timell and Jahn (378). In all instances, the yield of holocellulose diminished as the number of delignification treatments increased. Correspondingly, the acetone-solubility of the methanol-insoluble residue increased with the number of delignification treatments, a maximum solubility of 94 - 96% percent being attained. The holocelluloses from incompletely delignified pulps contained much larger amounts of hemicellulose than those more completely delignified. However, there seemed to be no direct correlation between the amount of pentosan in the holocellulose and the solubility of the holocellulose nitrate, i.e., a high content of pentosan did not necessarily indicate low solubility in acetone, although the solubility did increase with removal of appreciable amounts of pentosan. This increase in solubility was attributed to the removal of (nitrated) protolignin and not to the removal of pentosans which might form insoluble nitrates.

### 3. THE NITRATION OF HEMICELLULOSES AND RELATED SUBSTANCES

Nitrates of hemicellulosic material have often been prepared and, of these, the dinitrate of xylan has been the most carefully studied. The earliest reported nitration of xylan is that of Bader (16a, b) in 1895. Wood gum was treated with fuming nitric acid and yielded products which were not completely substituted. Will and Lenze (402) attempted to repeat the work of Bader, but varied the procedure by adding concentrated sulfuric acid to the nitric acid - xylan mixture. At no time was either the xylan or the product, which analyzed for xylan dinitrate, in solution in the acid mixture. Aqueous nitric acid, as would be expected, caused both hydrolysis and oxidation of xylan (192). Solochnik (366) was unable to get either a good yield or a completely substituted xylan dinitrate. Likewise, Husemann (209a), by means of a phosphonitric mixture, could introduce only 11.31% nitrogen into xylan. Xylan dinitrate requires a nitrogen content of 12.6%. Konkin and Rogovin (239a) obtained a ninety-two to ninety-eight percent yield of a nitrated straw xylan, but the content of nitrogen was lower than that for a dinitrate (10.2 - 10.9%). In this work also, a phosphonitric mixture was used. Other preparations of xylan dinitrate have been reported by Timell and Jahn (378) and Kagawa and Kondo (228). Rassow and Dorr (333) have studied the nitration of "pentosans", and Staudinger and coworkers (209c) the nitration of a "hemicellulose" which both Whistler (209c) and Husemann (209a) quote as being a xylan.

Since xylan is an important constituent in most hemicelluloses,

the problem of the solubility of its dinitrate is important in considerations of the solubility or non-solubility of nitrated wood. The information available is very contradictory. Will and Lenze (402) found that their xylan nitrate (from a sulfonitric mixture) was almost completely insoluble in organic solvents. Husemann's preparation from a phosphonitric mixture (209a) was likewise almost completely insoluble in acetone. Xylan nitrates present in the seed hairs of nitrated milkweed (365d) and nitrated paper birch wood (378) were also insoluble in acetone. Both the milkweed and paper birch wood had been nitrated with phosphonitric mixtures. By contrast, other authors have found that xylan nitrates are soluble in organic solvents. Rassow and Dorr (333) found that products which were free of hard, horny agglomerations (developed during the drying process) were soluble in the usual solvents for cellulose nitrates. The preparation of Konkin and Rogovin (239a) from phosphonitric mixtures was soluble in acetone to the extent of eighty percent. This result is completely at variance with those obtained by Husemann (209a), since the nitrogen contents of her preparations were higher than those of Konkin and Rogovin (239a). Both xylyns were prepared from wheat straw.

It was against this background of confusing results that Kagawa and Kondo (228)\* began their studies on xylan nitrates. These authors carried out a comparative study of the nitration of rice straw xylan and cellulose with both nitric acid and sulfonitric

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\* The author is grateful to Dr. K. Onodera of the Department of Biochemistry at The University of Kyoto for a translation of this paper.

mixtures. Surprisingly enough, it was found that xylan was nitrated more readily than cellulose by means of nitric acid. The xylan nitrates so prepared were also found to be more soluble than the cellulose preparations. It was also established that nitric acid is a more suitable agent for the nitration of xylan than are sulfonitric mixtures. On comparing these results with those obtained by Husemann (209a), the authors suggest that the discrepancies may be explained by the more ready hydrolysis of xylan as compared to cellulose. They further suggest that xylan may better be compared with pectins, with respect to its behaviour during nitration.

The behaviour on nitration and the solubility properties of the nitrates of hemicelluloses from many sources have been reported, and several isolated polymers have been studied. Husemann (209a) has nitrated an arabogalactan from larchwood. In spite of the fact that a phosphonitric mixture was used, the nitrate was severely degraded. Thus, its good solubility in organic solvents was not surprising. Mannans from various sources have also been nitrated. Husemann (209a) found that nitrated mannans from spruce wood were only partially soluble in acetone. A konjac mannan, which contained both glucose and glucuronic acid residues, was nitrated with various sulfonitric mixtures. The solubility of the mannan nitrate was found to be parallel to that of cellulose nitrates with similar nitrogen contents (179). The nitration of salep mannan (209b) with a phosphonitric mixture failed to give a completely substituted product; the highest nitrogen content

obtained was 12.5%. Mannan trinitrate requires a nitrogen content of 14.14%. Mannan from ivory nuts has been nitrated by both Kostevich (241) and Snyder and Timell (365c). Kostevich reported only partial solubility for his product, while Snyder and Timell found that their preparations were completely soluble in acetone. Meyer and Mark (287) have studied the viscosity and film-forming properties of nitrated mannan.

Mixtures of carbohydrate polymers (i.e., hemicelluloses which have not been separated into isolated "purified" polymers) also have been subjected to nitration. Watanabe (399c) has prepared the nitrates of the pentose portion of bagasse. The maximum nitrogen content obtained was 10.35%. The degree of nitration attained varied both with the degree of polymerization of the pentosans and with the composition of the sulfonitric mixture used. Acetone solubility of the products reached a maximum of 93.8% for the corresponding nitrogen content of 9.1%. Nitration of bagasse pentosan with acetonitric mixtures has also been carried out. Unfortunately, only the abstract of this paper was available and, there, no mention is made of the properties of these preparations except to indicate that they were very stable.

Attempts to analyze the waste liquors from various treatments of pulp have been reported. Brissaud (53c) was interested in the alkaline liquors reject from the viscose process for the production of rayon. Since the pulp was steeped in eighteen percent aqueous sodium hydroxide solution, it may be considered that most of the hemicellulose material had been extracted (66). Brissaud obtained

two fractions from the liquors. The first (A) consisted of the material readily precipitated on acidification of the alkaline solution, and was composed mainly of pentosans. The maximum nitrogen content introduced was 11.96%. It is interesting to note that nitrated A, from which xylose was isolated, was insoluble in the usual solvents for cellulose nitrate. Fraction B, which consisted of the material not readily precipitated from the alkaline solution, contained mainly lignin residues and hexosans. Both glucose and mannose were present, the latter in greater amount. The maximum nitrogen content of the nitrated B was 13.77%. Nitrated B was soluble in the usual solvents for cellulose nitrates.

Sadayoshi (346), Okawa and Fukatoma (308) and Watanabe (399b) were concerned with the alkaline liquors recovered after steeping of pulps for the mercerization process. Both sulfonitric and acetonitric mixtures were used by the latter authors to nitrate the material recovered from these liquors. The latter reagents yielded much more stable products. The solubility of the nitrated material in both acetone and methanol was greater than for nitrated celluloses.

Hess and Teves (178) investigated the methanol extract of a wood cellulose which had been nitrated with a phosphonitric mixture, but gave little information on the properties of the extract. Twenty-one percent of the extract was reported to be pentosan material.

Several carbohydrate polymers isolated from pectins and pectin-

containing materials have been nitrated and the properties of the nitrates studied. Schneider and Fritschi (354) have prepared a nitrated araban, and Vinogradova and coworkers (391) a nitrated galactan. The galactan trinitrate obtained by treatment of the isolated galactan with a phosphonitric mixture was soluble only to the extent of 4.5% in acetone, whereas a similarly-prepared cellulose nitrate was completely soluble.

In 1936, Henglein and Schneider (186) reported the results of a comprehensive study of the nitration of a pectic acid with concentrated nitric acid. The product contained 9.5% nitrogen which was only slightly less than that required for an oxy-pentosan dinitrate. It was soluble in water as well as in acetone. A hydrated pectin (containing araban) was also nitrated with a sulfonitric mixture. The product was soluble in the acid mixture. Degradation occurred, although to a lesser extent than that caused by nitric acid alone. The nitrated hydrated pectin was soluble in acetone, but not in water. Boch and Simmerl (228) similarly studied the nitration of dry pectin (polygalacturonic acid) with both anhydrous nitric acid and with sulfonitric mixtures. The reaction time was much shorter in the latter case and it was found that high molecular weight material did not dissolve in the nitrating acid. Also, as with cellulose, the solubility of the products increased with increasing nitrogen content, those with 8 - 10% nitrogen being soluble in acetone.

Speiser and Addy (367) nitrated apple pectin (also a polygalacturonic acid) with red fuming nitric acid. The yield was

excellent (90 - 95%) and the nitrogen contents were 9.3 - 9.5%, which corresponds to 1.6 - 1.8 nitrate groups per galacturonic acid unit. Although degradation did occur, it was considered not to be great.

The nitration of pectins by an acetone solution of dinitrogen pentoxide (353) has already been mentioned. The pectin nitrate was soluble in acetone. The pectin nitrated by gaseous dinitrogen pentoxide (393) was also soluble in acetone. The nitrogen content of the product of this reaction was 9.7 - 10%. Nitrated pectic acid, prepared in a similar manner, was not soluble in acetone.

There is one reported nitration of alginic acid (301) but, in the abstract, neither properties nor details of preparation are given.

#### E. THE NITRATION OF MISCELLANEOUS PLANT MATERIALS

Hemp fibres were nitrated in sulfonitric mixtures (315), and the products were found to be more stable than purified cotton cellulose nitrates. This was attributed to the greater accessibility of the nitrated hemp to the water wash.

Both birch bark (297) and bituminous coal (233) have been subjected to the action of hot, concentrated nitric acid. Although the main reaction was the expected oxidation, some nitrogen uptake did occur in each case. Both reactions were studied for their industrial importance.

Gralen, Berg and Svdeberg (157) used a phosphonitric mixture to nitrate Swedish cotton grass. The nitrated product was only

slightly soluble in organic solvents. Since the fibres were not lignified, but did contain some thirty percent of xylan, the non-solubility was attributed to the presence of nitrated hemicelluloses rather than protolignin. This is a sharp contrast to the suggested reason for the non-solubility of nitrated pulps and wood.

Friese (134) has used phosphonitric and acetonitric mixtures to nitrate straw, as well as wood, on a commercial scale.

The nitration of the seed hairs of milkweed (365d) has already been mentioned. Phosphonitric mixtures gave a product which was only partially soluble in methanol and partially soluble in acetone.

An extensive study of the action of nitric acid on plant seed hulls has been carried out by Kruger (245). After extraction with benzene-alcohol mixtures, and water, the hulls were subject to the action of fuming nitric acid at room temperature for twelve hours. As can be seen by reference to Tables XI and XII, the main reaction was one of pulping. The nitrogen taken up by the residue was almost totally in the form of the ester. Most of the lignin (based on the content of methoxyl) appeared in the acid-soluble material. The amount of material lost in the aqueous acid was large, indicating much degradative action.

#### F. THE NITRATION OF WHOLE WOOD

The nitration of whole wood as a preliminary step in the preparation of materials on which to conduct structural studies has, in the last decade, become a widely-used and important technic.

Treatment of wood with dilute nitric acid as a method of

TABLE XI

The Insoluble Residue from the Nitration of Plant Seed Hulls (245)

Source of Material	Yield (%)	Nitrogen Content (%)		Methoxyl (%)
		Total	Ester	
Coffee bean	62	12.2	12.2	0.7
Chestnut	58	-	11.2	0.8
Walnut	50	12.0	12.1	0.9
Hazelnut	48	12.2	12.0	1.0
Beechnut	47	11.7	11.6	0.9
Cherry kernel	47	12.1	12.0	0.9
Plum stone	45	-	11.3	1.2
Brazil nut	37	11.4	11.2	1.1
Horse chestnut	35	11.3	11.2	1.3

TABLE XII

Nitration of Plant Seed Hulls: Products Precipitated by Addition of Water to the Nitrating Acid (245)

Original Material			Material Recovered from Nitrating Acid			
Source	Lignin (%)	Methoxyl (%)	Yield (%)	Methoxyl (%)	Nitrogen Content (%)	
					Total	Ester
Coffee bean	27	5.7	20	6.8	9.9	5.5
Chestnut	32	2.2	13	3.1	9.6	9.1
Walnut	32	5.6	26	-	8.9	-
Hazelnut	35	5.3	23	5.7	9.9	5.6
Beechnut	37	4.0	19	-	-	6.5
Cherry kernel	36	7.2	29	-	8.5	5.4
Plum stone	33	7.5	28	10.3	8.8	5.7
Brazil nut	51	3.8	15	5.4	9.6	5.9
Horse chestnut	52	2.2	16	3.2	9.0	8.5

pulping has long been known. Although nitrogen-containing products (assumed to be nitrated lignin) have been isolated from the pulping liquors, the reaction was also oxidative as shown by an examination of the products of reaction (51b, 343, 350) and references in the section on lignin). Therefore, when nitration is carried out as the first step in a study of the chemistry of wood, reagents whose primary reaction is nitration, rather than oxidation, are chosen.

Much of the early work was carried out with a view to the development of procedures to be used on an industrial scale for the production of cellulose nitrates. This work will be discussed first. Hilpert, Kruger and Hechler (197) have studied the reaction of whole wood with concentrated nitric acid and with sulfonitric mixtures. The results with red beech and spruce wood are shown in Table XIII. The results suggest that most of the ligneous material was lost in the reaction mixture and that the product was cellulose nitrate rather than nitrated wood, i.e., the wood, in effect, was pulped. The material soluble in the acid solution was isolated and analyzed. Results are summarized in Table XIV.

Sulfonitric mixtures have been found to be much more useful than nitric acid alone as nitrating agents for wood. Data from several fairly comprehensive studies are available. Jahn and Coppick (93a, 218a) have studied the reactions of sulfonitric mixtures with a variety of woods. As can be seen from Table XV, the yields of nitrated softwoods were much higher than those of nitrated hardwoods. All of the products obtained by Jahn and

TABLE XIII

The Nitration of Red Beech and Spruce Woods (197)

Wood	Nitrating Agent	Reaction		Nitrogen Content (%)		Product Recovered by Dilution with Water		
		T(°C)	Time (hr)	Total	Ester	Yield (%)	Nitrogen Content (%)	
				Total	Ester			
Red beech	HNO <sub>3</sub>	5	3	-	9.1	25	9.3	6.4
	HNO <sub>3</sub>	20	2.4	12.0	11.9	23	9.2	6.4
Spruce	HNO <sub>3</sub>	5	3	-	8.9	23	9.8	6.6
	HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	10	2.4	11.6	11.5	-	-	-

TABLE XIV

The Nitration of Red Beech and Spruce Woods:  
Analysis of the Products Soluble in the Nitrating Acid (197)

Wood	Yield (%)	Nitrogen Content (%)		Methoxyl Content (%)
		Total	Ester	
Spruce	25	9.3	6.4	4.1
Red beech	23	9.2	6.4	-

TABLE XV

The Nitration of Wood with Sulfonitric Mixtures,  
According to Jahn and Coppick (93a, 218a)

Wood	Yield of Nitrated Product (%)	Nitrogen Content (%)
Aspen	102.6	10.8
Beech	112.4	10.27
Fire cherry	111.2	11.7
Red gum	128.0	10.8
Douglas fir	120.0	10.0
Southern pine	122.5	10.0
Western spruce	122.8	10.3
Idaho white pine	121.6	9.7
Eastern spruce	-	10.3

Coppick showed a certain degree of solubility in hot water, were more than ninety percent soluble in acetone and were soluble in other organic solvents. The soluble nitrates were fractionated by means of acetone-water mixtures and molecular weight determinations were carried out on the nitrated eastern spruce. Later work by Jahn (217) furnished evidence which suggested that chemical linkages between the components of wood were cleaved by the sulfo-mixtures (which were not anhydrous). It was still considered, however, that serious degradation of the acetone-soluble material had not occurred.

Lieser and Schaak (263) also have studied the reaction of

sprucewood with sulfonitric mixtures, containing varying amounts of water. The reaction proceeded very rapidly and was completed in two hours at 20° C. The weight of nitrated wood was dependent, of course, on the reaction temperature, the amount of nitrogen uptake and the loss to solution. The best yield was 159% of a product containing 11.8% nitrogen. Extraction of the nitrated wood with methanol caused some thirty percent of it to go into solution. The extracted material contained nine percent total and six percent ester nitrogen. In spite of the high content of ester nitrogen, the extracted material was considered to be essentially nitrated lignin. The amount of nitrated lignin extractable with alcohol increased with increasing reaction temperature.

A very comprehensive study of the nitration of whole wood by means of sulfonitric mixtures has been carried out by Hechler (183). However, since the object of this work was to produce nitrated carbohydrates suitable for explosive purposes, the chemistry of wood was not discussed by the author in relation to the results. It is interesting to note that the anhydrous sulfonitric mixtures used by Hechler did result in the production of products soluble in organic solvents. This is in contrast to the work of Friese and Furst (136) whose anhydrous acetonitric mixtures gave almost insoluble products. Since Hechler gives no viscosity data, it is hard to say whether the difference was caused by differences in decomposition of the components, the cleavage of linkages between components, or other factors.

Brissaud and Ronssin (54b) have conducted a series of experiments

on poplar and spruce woods nitrated with sulfonitric mixtures. The mixture used was such as would produce a cellulose nitrate containing 13.3 - 13.4% nitrogen, and was left in contact with the wood for one hour at 30° C. After a thorough washing with water the product was dried and analyzed. The nitrogen contents were 12.2% for spruce and 12.4% for poplar. After autoclaving, these nitrogen contents were, respectively, lowered and raised slightly. Yields of nitrated products were of the order of 110 - 120%, which was lowered by some 10 - 15% by treatment in the autoclave. The autoclaved product was soluble to the extent of fifteen percent in ether at 56° C. In a second series of experiments conducted by Brissaud and Ronssin (54b) on the same woods, similar results were obtained. The products obtained by reaction at 10° and 30° C. were slightly different as shown by the data in Table XVI. Brissaud and Ronssin (54b) have carried out similar experiments on poplar wood. Results of this work are also reported in Table XVI.

Kurschner and his coworkers have made a study of the reaction of wood with anhydrous solutions of nitric acid in ethanol. The original purpose of this work was to prepare purified pulps through removal of the nitrated protolignin by preferential solution. Separations of nitrated protolignin and nitrated hemicelluloses were successfully accomplished for a number of pulps and woods (248a, d, 249, 250). The method was therefore recommended as one useful for the quantitative determination of cellulose. Of all the plant materials studied, only defatted cacao (249) did not behave in

TABLE XVI

The Nitration of Wood with Sulfonitric Mixtures,  
According to Brissaud and Ronssin (54b)

Determination	Spruce Wood		Poplar Wood
	T = 10° C.	T = 30° C.	T = 30° C.
Yield of Nitrated Wood	65 - 70	67.5	55 - 60
Nitrogen Content (%)	12.2	10.91	11.1 - (12.4)
Sol. of Nitrated Wood in Alcohol (%)	good	good	14 *
Nitrogen Content of the Residue (%)	13.35	11.76	11.70
Sol. of Residue in Acetone	nil	nil	-
Nitrogen Content after Treatment with Acetone	11.34	11.9	-

\* A fraction representing 2.4% of the native wood separated from the methanol solution on cooling. On evaporation of the remaining solution a further fraction, representing 11.6% of the weight of nitrated wood, was isolated.

a satisfactory manner. The determination of cellulose in this substance was successful when acetic acid was substituted for ethanol as solvent.

Subsequent work, however, was concerned with a study of the nitrated lignin which was extracted, the studies again embracing a wide variety of woods and foodstuffs (248a, f, i, 252b, 253, 296). This work was undertaken to gather evidence as to the carbohydrate or aromatic nature of protolignin (248i). The reagent chosen—an anhydrous mixture of nitric acid and ethyl alcohol—was assumed to react without cyclization of methylated carbohydrates, thus giving the substances which are isolated as lignin. Kurschner considers that the polymerization would proceed in the manner of a chain reaction, and would be initiated by the presence of a trace of water.

Nitrated pine lignin from pine protolignin was obtained in twenty-two percent yield. It, and other lignins, were isolated in a crystalline form (248a, 251a). Nitrogen contents of these nitrated lignins varied from 9.81 - 15.6% of nitro ( $\text{NO}_2$ ) groups. Analysis of the crystalline nitrated lignin from pine was: 9.91% methoxyl; 3.3% total nitrogen. The almost certain presence of the n-propylbenzene nucleus in these nitrated lignins was also indicated. It is of interest to note here that Nyhof (305) was unable to repeat Kurschner's preparation of a crystalline nitrated lignin.

Products obtained by nitrating protolignin in situ, and those obtained by the nitration of isolated lignins were compared by

Kurschner and Peikert (251a). Analytical data for these preparations are shown in Table XVII. The nitrated lignins were obtained by addition of water to the alcoholic solution. Yields were fifteen to seventeen percent. It was apparent that methanol reacted with the lignin, as evidenced by the increased methoxyl contents. All of the nitrogen was present in the form of C-nitro groups.

TABLE XVII

The Nitration of Spruce Lignin and Protolignin with  
Nitric Acid - Ethanol Solutions (251a)

Type of Lignin	Solvent During Nitration	Content of Nitrogen (%)		Methoxyl Content (%)
		Total	Nitro	
Protolignin	Methanol	3.08	3.05	15.35
Protolignin	Ethanol	3.60	3.33	10.07
HCl lignin	Methanol	3.27	3.23	14.14
HCl lignin	Ethanol	3.26	3.18	9.37
Methylated 1 or 2 X	-	2.56	2.57	21.96
Methylated 3 or 4 X	-	2.79	2.82	21.32

Further proof for the aromatic nature of lignin was obtained from a study of the properties of the crystalline nitrated spruce protolignin (251b). The isolated nitrated lignin was reduced, diazotized and treated with a solution of  $\beta$ -naphthol. A red color, characteristic of the reaction of a diazotized primary aromatic

amine, was produced. Again, all of the nitrogen taken up by the protolignin, and present in the isolated nitrated lignin, was in the form of nitro groups (248b). Analytical data are reproduced in Table XVII.

TABLE XVIII  
Analysis of Nitrated Lignins and Protolignin (251b)

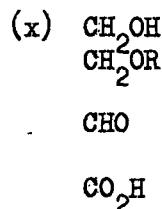
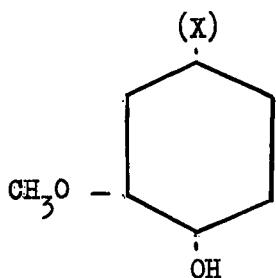
Type of Lignin	Solvent During Nitration	Content of Nitrogen (%)	
		Total	Nitro
Protolignin (spruce)	Ethanol	3.55-3.64	3.27-3.37
" "	Methanol	3.05-3.1	2.98-3.12
Technical lignin	-	3.21-3.37	3.12-3.62

Yet further proof of the aromatic nature of protolignins was obtained by work on spruce and beech woods. The wood used was dried for eight hours at 105° C., then half an hour at each of 120° and 110° C. Both alcohol and nitric acid were thoroughly dried, the latter to a state where it contained small amounts of dinitrogen pentoxide (248i).

As the reaction proceeded, at room temperature, the wood changed color to orange-red or brown, and the nitrating solution became yellow. Heating at 72° for two hours had the effect of lightening the color of the wood, while the solution became much darker. On working up the reaction mixture, both the residue and the extract

(precipitated from solution by the addition of water) were light yellow. By comparison of the amount of nitrated isolated lignin (assumed to be formed from protolignin) with the amount of lignin isolated by the usual methods, Kirschner (248i) calculated that approximately two-thirds of spruce lignin and six-sevenths of beech lignin were produced from carbohydrate material during isolation.

Gustafsson and coworkers (164, 165) have investigated the nitration of wood with ethereal solutions of nitric acid containing sodium nitrite. It was known that such treatment should result in the production of dinitroguaiacol. The presence of the lower oxides of nitrogen in the mixture gave increased yields of this substance. All four woods investigated (Picea excelsa, Pinus silvestres, Betula verrucosa and Alnus glutinosa), yielded dinitroquaiacol. From control experiments with model compounds, it was concluded that only compounds with the structure



will react to form this latter compound. Introduction of a methoxyl or carbon group ortho to the free hydroxyl (e.g. as in syringaldehyde) completely blocked its formation. It was considered that no methoxyl group was removed but that only end groups of protolignin can give rise to dinitroquaiacol.

Jayme and Harders - Steinhauser (220) treated beechwood cross sections with nitrogen dioxide. Since lignified fibres were

colored a deep yellow whereas delignified fibres showed no color, the reaction was considered to be diagnostic for protolignin.

Friese and coworkers (134, 136, 137) were among the first to use nitrated whole wood from which to isolate the components in a state suitable to serve as starting materials for structure studies. The use of anhydrous nitrating agents would seem to be necessary in order to avoid decomposition. For this reason, Friese (134, 136) studied the reaction of pine wood with a number of reagents which had proved useful in the nitration of cellulose. A brief summary of the results is shown in Table XIX. Sulfonitric mixtures caused extensive degradation and loss of material to the nitrating medium. Both acetyl nitrate and mixtures of nitric, phosphoric and acetic acids gave a much improved yield of product, but the loss to solution was still high and the amount of nitrogen introduced was rather small. Replacement of acetic acid by acetic anhydride gave results which were again an improvement but still not entirely satisfactory. Mixtures of nitric acid with phosphoric acid, and with acetic acid and acetic anhydride were by far the most satisfactory. Yields and nitrogen contents of the products were high and the fibre structure of the original wood was retained. Loss of methoxyl was at a minimum also. The acetonitric mixture was the most satisfactory of all tested, for little decomposition of the wood occurred and acetyl groups were taken up to a negligible extent. However, the solubility of the product in acetone was only six percent and the solubility in methanol was also very slight. These results are in direct contrast with the ready solubility of nitrated Tornesch lignin in methanol.

TABLE XIX  
The Nitration of Extractive-Free Pine Wood (136)

Mixture Used for Nitration	Reaction		Yield of Nitrated Wood (%) <sup>b</sup>	Nitrogen Content (%)			Methoxyl Content (%)	Fibre Structure of Product	Amount of Material Recovered from Nitrating Mixture (%)
	t (Hr.)	T (°C.)		Total	Ester	Nitro			
HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	4	20	55	8.45	7.1	1.35	-	lost	1.05
HNO <sub>3</sub> /H <sub>3</sub> PO <sub>4</sub> /HOAc	6-8	20	105	4.5	2.6	1.9	3.3	lost	1.8
HNO <sub>3</sub> /H <sub>3</sub> PO <sub>4</sub> /Ac <sub>2</sub> O	6-8	20	127	8.0	5.5	2.5	3.8	lost	nil
HNO <sub>3</sub> /H <sub>3</sub> PO <sub>4</sub>	4	20	151	12.4	9.9	2.5	3.6	retained	nil
HNO <sub>3</sub> /Ac <sub>2</sub> O/HOAc	8	room	165	12.5	10.1	2.4	3.7	retained	3.8
AcONO <sub>2</sub> /Ac <sub>2</sub> O <sup>a</sup>	-	0	106.5	5.9	3.4	2.5	5.0	retained	0.4

a. The reagent was prepared from dinitrogen pentoxide and acetic anhydride. Beech wood was used as the starting material.

b. Calculated as the ratio of weight of the product / weight of wood originally used.

Friese and Ludecke (137) made use of a mixture of nitric and acetic acid to nitrate whole wood. It was hoped that this reagent would bring about the preferential nitration of protolignin while leaving intact the aliphatic hydroxyl groups of the carbohydrate materials. The reaction was allowed to proceed for some twenty hours at temperatures below 25° C. One hundred grams of pinewood so-treated gave ninety-six grams of residue insoluble in the nitrating acid. The insoluble residue from one hundred grams of beechwood weighed eighty-six grams. The residues from several preparations with pinewood had an almost constant content of nitrogen of 2.1%. This residue was insoluble in water and in methanol as well as in the nitrating mixture. The material soluble in the nitrating acid was recovered in the manner shown in the flow sheet. A further five grams of material was recovered from the

Reaction Solution	
	conc. <u>in vacuo</u> add water
residue	solution
1.7 g. 5.85% N	3.9 g. 3.1% N

water used to wash the residue. The nitrogen content of this fraction was 3.5%.

Traynard and Robert (336, 383a) have also attempted to effect a separation of carbohydrate and protolignin in wood through selective nitration of the latter component. The acetonitric mixture chosen was different from most of those used in that it had a very low concentration of nitric acid. Poplar wood was allowed to react

with the acid mixture for four hours at 40° C. Eighteen grams of a yellow, crystalline material was isolated from the reaction medium. This was assumed to be a nitrated lignin. It was insoluble in water and non-polar solvents such as ether and benzene, but was soluble in acetone, ethanol and other oxygen-containing solvents. Although the infrared spectrum was identical to that reported by other workers, no decision of its relationship to protolignin could be made. Analytical results were: methoxyl, 8.2%, which is low for lignin and showed a loss from the original wood; nitrogen, 3.7%, not present as the ester. Tests for aromatic nitro groups seemed to be inconclusive, as only a brown color was obtained when a reduced and diazotized material was treated with  $\beta$ -naphthol. On the basis of this and other analytical and experimental data not summarized here, it was concluded that the main reaction had been oxidation, although some nitration had occurred. The consumption of more nitric acid than could be accounted for in the extracted fraction indicated that the non-soluble residue had also been attacked. Traynard and his coworkers (382) have recently developed this delignification technic into a method for the detection of protolignin in microtome cross-sections of wood.

More recently, Brissaud and Ronssin (54b) carried out a series of experiments on the nitration of wood. After preliminary work with sulfonitric mixtures, they turned to the use of acetonitric mixtures as being more gentle in action and therefore offering better opportunities for study of the nitration products. Spruce-

wood meal, which had been dried for three hours at 100° C. was treated for four hours at 0 - 6° C. The ratio of wood to nitrating mixture was 1:25. At the end of the reaction the solid product was washed with water, dried and analyzed. It was yellow in color, and retained the appearance of the original wood. The yield was 156%, or 97% of the theoretical value. The content of nitrogen was 11.75%. Previous work had established that the solubility of the nitrated wood in acetone was enhanced by pre-treatment with boiling water. Therefore, after the usual extractions with methanol, and with acetone, the residue was treated with boiling water. After this cycle of extractions (methanol, acetone, hot water), more of the residue was soluble in methanol. Each of several such cycles yielded new fractions, although in decreasing amounts for each successive set of treatments. A plot of the amount of fraction isolated versus the total time of treatment with boiling water was asymptotic. This indicated that an infinite number of such cycles would be required before complete solubility of the wood was achieved!

Brissaud and Ronssin examined the isolated fractions in some detail. The dissolved material was highly degraded, as indicated by the isolation of oxalic acid. Thus, it was assumed that some of the nitrated lignin had been attacked. The alcohol extracts were dark brown in color and the brown powders isolated had contents of 7.8 - 9% total and 5.5 - 6.6% ester nitrogen. The nitrogen content decreased with each successive extraction. The presence of both ester (O-nitro) and C-nitro groups was also indicated by infra

red spectroscopy. The methanol extract could be further fractionated by extraction with water. The water-soluble fraction contained 12.8% total nitrogen and 6.86% ester nitrogen. The material extracted from nitrated wood by treatment with methanol (approximately fifteen percent of the nitrated wood) thus seemed to consist of a mixture of low molecular weight carbohydrate material and nitrated lignin.

Treatment of the residues with acetone (after extraction by both methanol and hot water) resulted in the production of a very viscous solution from which fine, voluminous filaments separated on addition of water. These contained 12 - 12.5% nitrogen. This solid could be further divided into fractions by treatment with methanol. The material soluble in methanol contained some eight percent nitrogen. The nitrogen content of the residue from this extraction rose to 13 - 13.6%. It was almost entirely hemicellulosic in content. Although a total of forty-five percent of the nitrated wood was finally obtained in acetone solution, the degree of polymerization of the extracts fell rapidly with each successive cycle.

The fraction recovered from the aqueous acetone solution contained some 9 - 10% nitrogen.

Replacement of treatment with hot water by treatment in an autoclave resulted only in more drastic degradation of the nitrated products.

This work shows that clean separation of the nitrated components is very difficult to attain. Most of the extracts contained both nitrated carbohydrate and nitrated lignin substances.

Phosphonitric mixtures have been used even more extensively than acetonitric mixtures in the preparation of nitrated whole wood. Early experiments were carried out by Gralen and Ranby (158). Maximum acetone solubility of the nitrated wood was forty percent. However, Mitchell (292a) seems to have been the first to study this reaction thoroughly. Mitchell nitrated wood (southern pine in the form of shavings or ground wood) and pulps (ten grams) with eight hundred grams of nitrating mixture. The reaction took place at 20° C. After turning dark brown when first added to the nitrating mixture, the wood was again light in color by the end of the reaction period. Reaction times of less than twenty-four hours resulted in products which were incompletely soluble in ethyl acetate. The yields of product varied from 120 - 130%, and nitrogen contents were thirteen percent. The nitrated wood was stable to storage. Nitration of the same wood with acetonitric mixtures with reaction times as long as one hundred and forty hours gave products which were soluble in acetone only to the extent of thirty-seven percent. Sulfonitric mixtures yielded products which were completely soluble in acetone, but were incompletely substituted and degraded.

Mitchell considered that the better solubility properties of wood nitrated with a phosphonitric mixture over those nitrated with an acetonitric mixture were due to the "disruptive action" of the former on the cellulose-protolignin linkage. This disruptive action, however, was considered not to cause appreciable cleavage of the cellulose chains themselves. To achieve a high degree of solubility of nitrated wood, not only must carbohydrate-protolignin

bonds be cleaved, but the protolignin must also be destroyed. Mitchell attributed this to the fact that, although nitration may be complete, ligneous residues on the surface of the cellulose nitrate fibres hinder the movement of the swollen nitrate outward to the solvent. It was assumed that, while acetonitric mixtures give highly nitrated products, the destructive action on protolignin is not enough to free the cellulose nitrates so that they may enter into solution. The nature of the disruptive and destructive reactions is not known, although Timell (377b) believes that they are oxidative. Thus it is seen that the lack of solubility of highly nitrated wood is attributed to the presence of protolignin. Timell (see below) has recently provided some striking proof of the validity of these views. The success of any nitration procedure also depends upon the treatment of the wood before reaction. It must be such that an "open structure" is maintained. This is an effect which has often been noted in reactions with cellulose.

Nitrated protolignin was removed from the nitrated wood by extraction with methanol, nitrated hemicelluloses being removed at the same time. At the end of the extraction the insoluble residue was still yellow. The material recovered from the methanol extracts was dark brown and brittle.

Further studies by Alexander and Mitchell (5) on western hemlock wood and various pulps have confirmed the observation (62, 292a, 378) that longer reaction times are required to ensure satisfactory solubility of highly lignified materials.

Other comprehensive studies on the reaction of phosphonitric mixtures have been carried out by Timell and his coworkers. The object of this work has been to separate cellulose from wood in a non-degraded state. Timell and Jahn (378) conducted such a study on paper birch wood. The reaction temperature was 6° C. The effect of time of reaction on the solubility of the products is shown in Table XX. Nitrogen contents of the products, which were cellulose nitrates, were 13.33 - 13.39%.

TABLE XX

Acetone-Solubility of Methane-Extracted, Nitrated Paper Birch Wood (378)

Reaction Time (Hr.)	Yield of Nitrated Product (%)	Solubility in Acetone (%)
1	112.2	26.6
3	102.5	33.0
5	97.8	41.4
9	93.7	56.8
24	86.4	63.9
24	-	-
24	87.0	60.8
48	84.4	72.3

Snyder and Timell (365a, b, c) have recently reported that similar considerations apply to the nitration of balsam fir. A reaction time of seventy-two hours at 17° C. was chosen as the results (Table XXI) indicated that the amount of nitrated cellulose recoverable from the methanol-extracted product became constant at that time. Under the experimental conditions given, seven percent of the nitrated wood was insoluble in acetone, and fourteen percent of the acetone-soluble fraction remained in solution after dilution with water. Snyder and Timell were also surprised to find that most of the xylose was in the acetone-soluble fraction (Table XXII). (Xylan dinitrate was considered to be insoluble in organic solvents). However, the amount of xylan in the acetone-soluble fraction was small (0.9%). There was 7.4% pentosan in the original wood.

In agreement with the observation that optimum conditions for each species must be determined experimentally, Timell (377b) found that the optimum reaction time for white spruce was 22.5 hr. It is also interesting to note that the particle size of the wood had some influence on the yield of nitrated product (cellulose nitrate), as shown in Table XXIII. Less xylan (as the nitrate) was present in the cellulose nitrate fraction than was originally associated with  $\alpha$ -cellulose isolated in the usual manner from holocellulose. This again was attributed to the lack of solubility of xylan dinitrate.

Both the sapwood and heartwood of white birchwood have been nitrated and fractionated by Timell (377e). The main difference was the slightly higher (approximately two percent) yield of cellulose

TABLE XXI

The Nitration of Balsam Fir Wood at 17° C. (35b).

Reaction Time (hr.)	Nitrated Wood (%)	Cellulose * (%)
6	137.9	11.3
12	132.9	13.6
18	122.2	28.6
24	121.5	34.7
36	116.0	41.1
48	114.0	44.3
52	110.9	48.6
58	110.9	48.0
64	109.7	49.0
72	111.0	49.2
76	110.2	48.5
82	110.2	48.5
96	109.8	48.4
120	106.9	46.0

\* The methanol-insoluble, acetone-soluble material recovered on addition of water to the acetone solutions.

TABLE XXII

Sugar Residues Present in the Various Fractions from  
Nitrated Balsam Fir Wood (365b)

Fraction	Glucose	Mannose	Galactose	Arabinose	Xylose	Uronic Acid
Original wood	+	+	+	+	+	+
Used nitrating acid						
Acetone-soluble portion	+	+			+	
Acetone-in-soluble portion	+	+	+			+
Methanol extract	+	+				
Water-acetone soluble portion	+	+				

TABLE XXIII

Effect of Particle Size on the Yield of Cellulose Nitrate Obtained from White Spruce (377b)

Mesh size	Yield (%) *
20-40	22.4
40-60	20.7
60-80	20.1
80-100	29.5

\* Yield of cellulose nitrate.

from the sapwood. Reaction times as short as two hours (at 17° C.) sufficed to give the constant amount of cellulose expected from this method, but degradation set in at an early stage; it was evident at the ten-hour point. An isolated birch holocellulose began to show marked degradation after only five hours' reaction time. In turn, the isolated birch cellulose remained intact for only two hours, and some denitration occurred. These different results led Timell to investigate the degradation as a function of the removal of lignin. These investigations took the form of viscosity measurements on a cellulose nitrated, (a) in a spent acid mixture; (b) in the presence of added spruce glycol lignin; (c) in a fresh acid mixture. Surprisingly, where lignin was present (i.e., in the first two mixtures) degradation was slower and less complete, although the same for both, than when fresh acid was used for the nitration. These results indicate that lignin has a stabilizing influence on the cellulose. The isolated lignin imparted the same red color to the acid mixture as did the protolignin from whole wood. Since little is known concerning the nature of protolignin, it is probably not safe to hazard a guess as to its effect on the degradation. However, as Timell pointed out, the different stabilities of the various woods nitrated by him could be explained by the variety of protolignins present.

The nitration of Eucalyptus regnans with phosphonitric mixtures has been reported by Emery and Cohen (118). Even after extraction with methanol, their products were cream-colored and not entirely soluble in acetone, an indication of the presence of nitrated protolignin.

Aspen, as well as sprucewood, have been studied by Heuser and Jorgensen (193). The results were essentially the same as found by previous workers.

Phosphonitric mixtures have also been used (2a) to study the various fractions obtained when spruce and fir wood were hydrolyzed with water.

**III. EXPERIMENTAL**

#### A. THE PREPARATION OF ANHYDROUS NITRIC ACID

Anhydrous nitric acid was prepared by the method of Vogel (393); preliminary treatment of commercially available nitric acid with urea (to remove nitrous oxides) was followed by distillation from twice its volume of concentrated sulfuric acid. Both yellow fuming and ordinary concentrated nitric acids were used as starting materials. During distillation (in the all-glass apparatus shown in Plate I) a pressure of twenty-five to forty millimeters of mercury was maintained by means of a water pump.

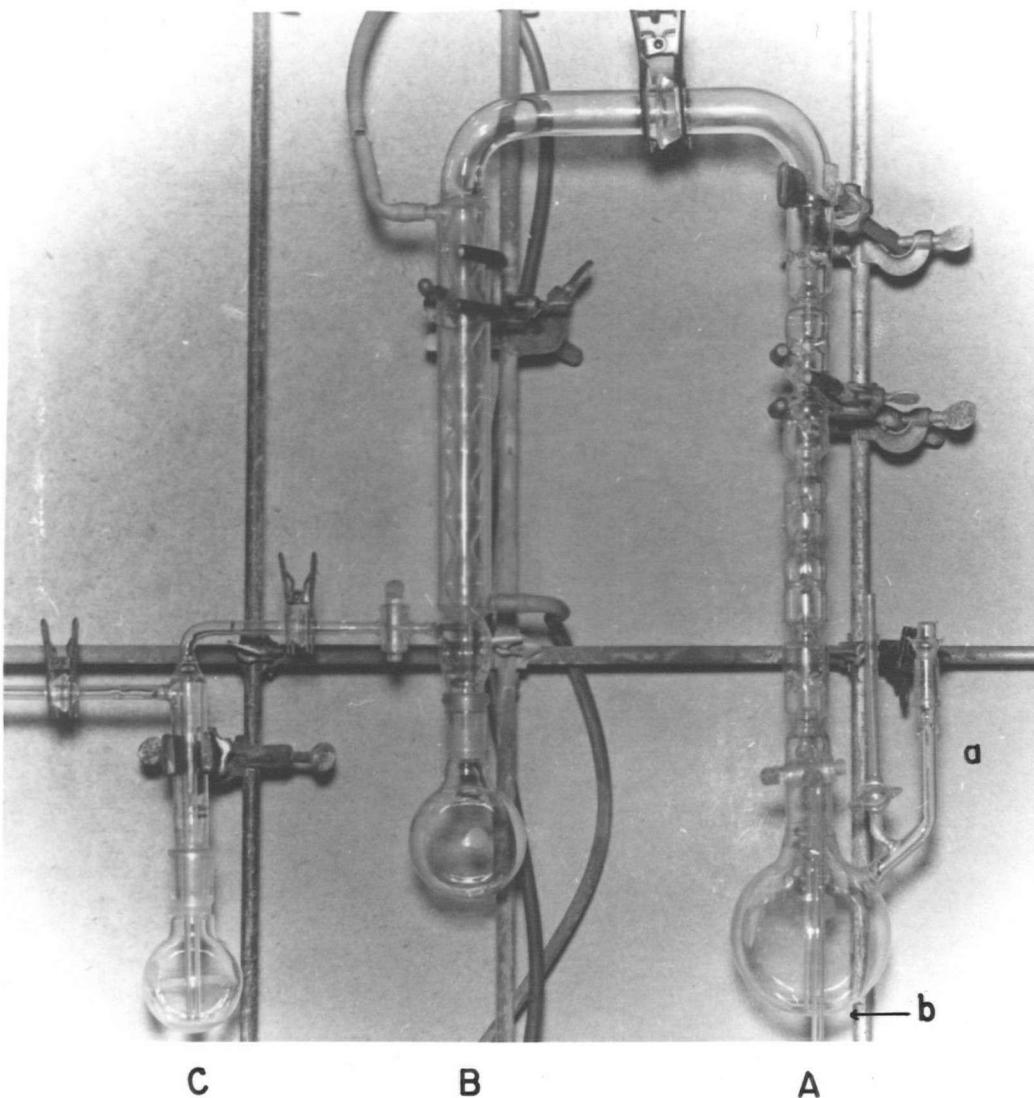
The yield of water-white distillate from 125 ml. of yellow fuming acid was 80 - 90 ml., while 50 - 60 ml. were obtained from an equal volume of the concentrated acid. Titration showed the acidity to be over one hundred per cent. This acid did not keep well at 0° C. in the dark, but soon took on a yellow tinge. However, it was stored successfully by preparing sealed tubes, each containing 15 ml. of the acid, which were kept in dry ice-acetone until use. To ensure that the nitric acid remained anhydrous, and for safety in handling, the sealed tubes were opened while the acid was still frozen. The opened tubes were then placed in a desiccator, where they remained until all solid had melted. The acid was then ready for use.

#### B. THE PREPARATION OF DINITROGEN PENTOXIDE

Dinitrogen pentoxide was prepared from nitric acid and phosphorus pentoxide in the presence of ozone. The reaction train itself (Plate II) is a modification of that described by Gruenhut, et al (163),

PLATE I

Still for the Preparation of Nitric Acid



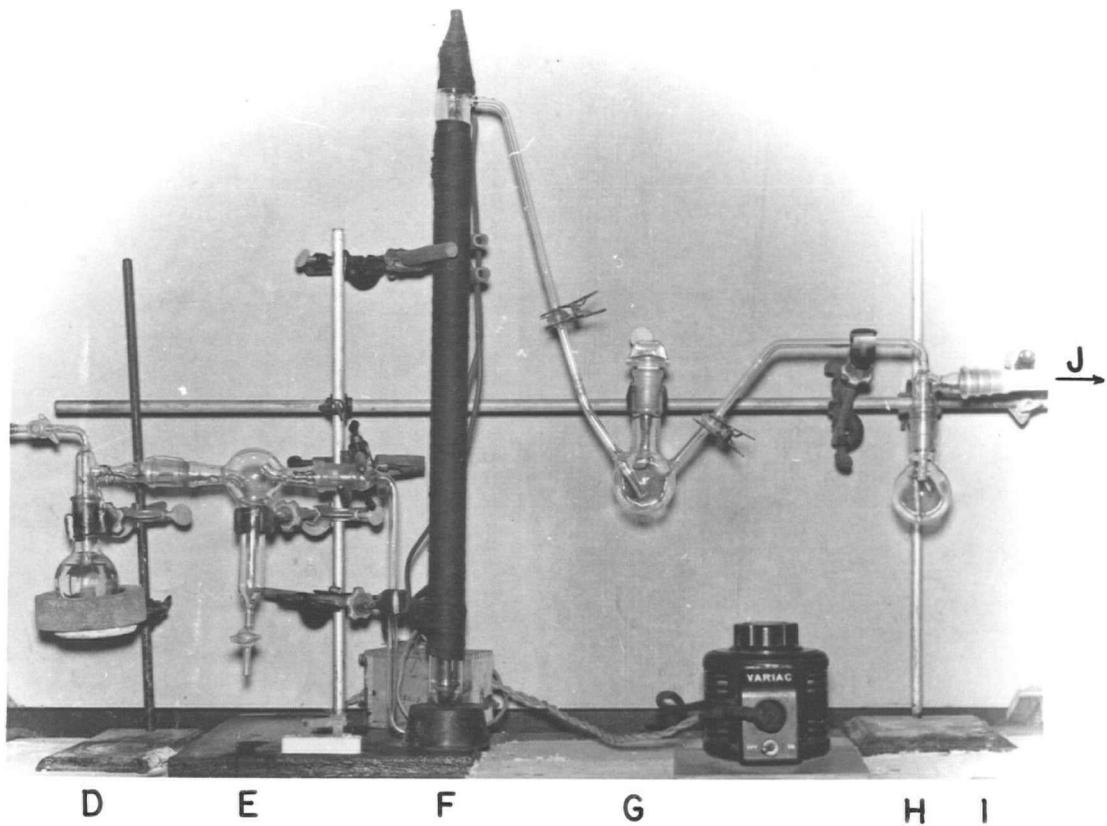
- A. Still pot, with column and attachments for filling (a) and emptying by siphon (b).
- B. Receiver: cooled in ice water.
- C. Trap: cooled in ice water-calcium chloride. Not shown: soda lime tube and dry ice trap, interspersed between C and the pump.

while the silent discharge tube (ozoniser) was built to the specifications given by Bonner (48).

The apparatus was set up as shown with a small wad of glass wool in the receiver (H), and dry air was blown through for some time. When it was deemed that all the moist air had been displaced, the flow was interrupted. The reaction flask (G) was then charged with specially prepared nitric acid (15 ml.) and immediately immersed in dry ice - acetone. When the acid had completely solidified, several grams of phosphorus pentoxide were quickly added to G and the generation of ozone (from air) was initiated. When the dry ice - acetone bath was transferred to H, the nitric acid slowly melted and the reaction proceeded spontaneously. Only occasionally was it necessary to control the rate of evolution of dinitrogen pentoxide by application of an ice bath to G. The dinitrogen pentoxide, which was entrained in the stream of air, was frozen out in H. After approximately two hours, the evolution of dinitrogen pentoxide almost ceased, but could be made to continue by brief stirring of the reaction mixture at intervals of twenty to thirty minutes. The ozonizer was generally kept in operation for an hour after evolution of dinitrogen pentoxide had ceased, making a total preparation time of five to six hours. At the end of this time, the ozonizer was turned off and dry air was passed through the system for a few minutes to sweep out excess ozone. The white, crystalline dinitrogen pentoxide (4 - 4.5 g.) was distilled once before use; the receiver (H) was attached to one leg of the distillation loop (Plate III), a second flask (K) (containing a small wad of dry glass wool) was attached to the other leg and the whole system evacuated to a pressure

PLATE II

Apparatus for the Preparation of Dinitrogen Pentoxide



D. Drying tower ( $H_2SO_4$ ) through which air was slowly bubbled.

E. Trap.

F. Silent discharge tube. This was charged through a Ford coil which, in turn, received a small direct current by connection through a variac (set at 5) which was plugged into a 110 V line.

G. Reaction flask: 100 ml.  $\frac{B}{2}$  24/40 flask.

H. Receiver: 100 ml.  $\frac{B}{2}$  24/40 flask.

I. Soda lime trap.

J. Gas vent.

of one to two millimeters of mercury. After closing the stopcock, the dry ice - acetone bath was transferred to K and the whole apparatus left at room temperature for an hour. The dinitrogen pentoxide, which solidified in K, was ready for use after air was admitted to the system.

#### C. THE NITRATION REACTION

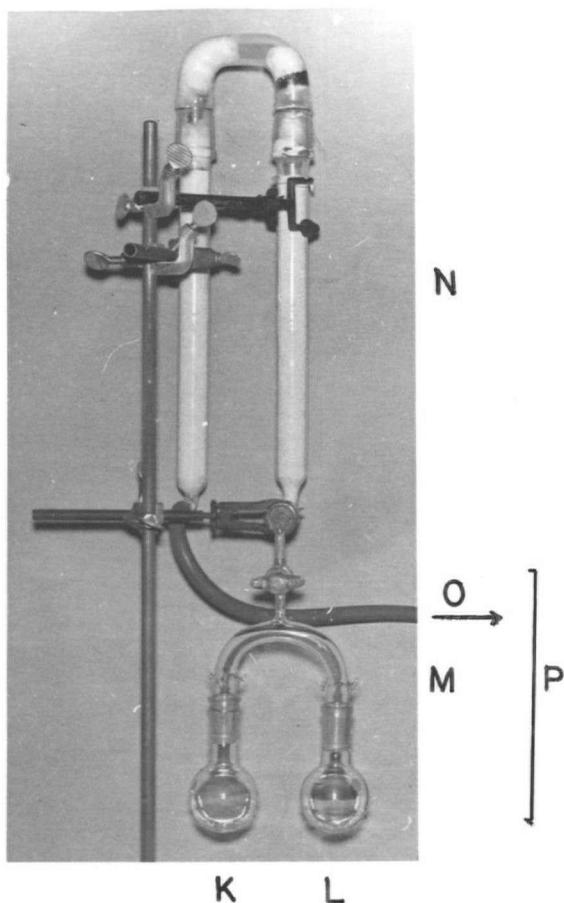
The apparatus (Plate III) and the freeze-distillation method of handling dinitrogen pentoxide were described by Vollmert (393).

The substance to be nitrated (50 - 200 mg.) was weighed into a dry, tared vial which, in turn, was placed in a 100 ml. S24/40 flask of special construction (see Appendix I). As many as six vials could be accommodated in one flask. This reaction flask was then attached to the distillation loop (L) in place of the original receiver (H). The system was again brought to a pressure of one to two millimeters of mercury and the stopcock then closed. From this point, the procedure varied. In some cases the cooling bath was removed from K and the distillation loop was placed in a refrigerator at  $1 \pm 2^\circ$  C., to be left thus for the duration of the reaction. In other instances, the dinitrogen pentoxide was freeze-distilled into L (by transfer of the cooling flask) before the reaction was allowed to proceed at  $1 \pm 2^\circ$  C.

The reaction was stopped at the desired time by re-immersion of K in dry ice - acetone. The system was generally allowed to stand overnight thus, in order to remove excess dinitrogen pentoxide and/or nitric acid. Further removal of excess dinitrogen pentoxide was accomplished by subjecting the system to evacuation (at a pressure of

PLATE III

Apparatus Used for the Nitration Reaction



- K. Flask (100 ml. 24/40, heavy-walled), containing solid dinitrogen pentoxide.
- L. Flask (as for K), containing the material to be nitrated.
- M. Distillation loop with stopcock.
- N. Trap: towers of soda lime.
- O. To dry ice-acetone trap and rotary oil pump.
- P. Assembly which may be detached and kept in the refrigerator during the reaction period.

one to two millimeters of mercury) for half an hour, with the stopcock open. The system was then opened to the air and the nitrated product(s) removed and weighed. The weight of the product so-treated was used in calculating all initial yields and weight increases, as reported in the next section.

#### D. THE PREPARATION OF STARTING MATERIALS \*

##### 1. Vanillic Acid

A small sample of vanillic acid was prepared from vanillin by oxidation with silver oxide (318b).

##### 2. Extractive-Free Western Red Cedar Heartwood Meal \*\*

All wood used in the following experiments was taken from one sound, second-growth tree, estimated to be forty to fifty years old. A three-foot length of the butt, growing approximately nine feet from the ground, was freed of bark and light-colored sapwood. The heartwood splinters derived from the remaining wood were air-dried and then reduced to meal in a Wiley mill. Separation of the 42 - 80 mesh fraction was followed by its exhaustive extraction with acetone, in a Soxhlet extractor. This extractive-free wood meal, brought to constant weight in vacuo over phosphorus pentoxide, was used for all experimental work without further treatment.

##### 3. Lignin

Lignin was prepared by treatment of extractive-free wood meal

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\* See Appendix II for a description of other substances used in the nitration experiments.

\*\* Felling of the tree, and the reduction of the heartwood to meal, was carried out by Dr. L.D. Hayward.

with seventy-two percent sulfuric acid according to the Tappi standard method T13m-54.

4. Holocellulose

Holocellulose was prepared from extractive-free wood meal by four treatments at hourly intervals with sodium chlorite - acetic acid. The directions given by Wise, Murphy and D'Addieco (407) were followed.

E. OTHER NITRATIONS

1. Cellulose

Cellulose (see Appendix II) was nitrated according to the method of Bennett and Timell (32a).

2. Wood

Extractive-free western red cedar heartwood meal was nitrated according to the method of Friese and Furst (136). One gram of the wood meal was stirred with a mixture of acetic anhydride (9 ml.), glacial acetic acid (1.2 ml.) and nitric acid (2 ml. of acid prepared as described above). The reaction proceeded for eight hours at room temperature. At the end of the first hour, the wood had turned red-brown and the mixture was just warm to the hand. At the end of two hours, the wood had swelled so that there was little "free" liquid. The reaction mixture was allowed to stand overnight (unstirred), and was then filtered on a sintered glass funnel. The residue was washed with glacial acetic acid followed by a little cold methanol. Both wash liquids were yellow, and a precipitate formed on addition of water to the glacial acetic acid (filtrate). The

product was brought to constant weight in vacuo over phosphorus pentoxide and solid potassium hydroxide.

#### F. ANALYTICAL METHODS

##### 1. The Determination of Nitrogen

Total nitrogen was determined on a micro scale both by a modified Dumas method (302) and by a modified Kjeldahl method (56).

Ester nitrogen was determined by the nitrometer method, on a semimicro scale, following the procedure of Elving and McElroy (117).

##### 2. The Determination of Methoxyl

Methoxyl contents were determined by the method of Clark (86).

##### 3. Viscosity Measurements

Viscosities of ethyl acetate solutions of cellulose nitrate were determined in a commercially available (Exax) viscometer of the Cannon - Fenske type (72). Intrinsic viscosities were calculated from single viscosity readings by the Baker (18, 265) equation. Intrinsic viscosities were corrected for nitrogen content of the nitrated celluloses by means of the equation of Lindsley and Frank (266).

#### **IV. DISCUSSION OF THE RESULTS**

#### A. INTRODUCTION

##### 1. THE OBJECT OF THE WORK

The present work on the nitration of whole wood was designed to be the preliminary step in a study of the hemicellulose component of western red cedar heartwood. However, inasmuch as the hemicelluloses of wood are very intimately associated with both the protolignin and the cellulose components (so much so as to make difficult the establishment of a suitable system of nomenclature!), any study of such a component must first be preceded by a study of the method of isolation of the intact component.

The only available technic which, so far, has proved useful for this purpose is the preparation of derivatives of wood which are soluble in organic solvents. Separation of the individual components by solution technics is then sometimes possible. As described in the historical survey, the derivative which has been found most suitable is that formed when wood is treated with a suitable nitrating mixture. For this reason, attention was first directed towards a study of the behaviour of wood on nitration, so that a firm basis might be established on which to conduct further solubility and structural studies.

##### 2. THE CHOICE OF NITRATING AGENT

It will have been seen from the historical survey that, although both aceto- and phosphonitric mixtures are powerful nitrating agents, their use to prepare nitrated material on which to conduct a study of the chemistry of wood, is limited. Acetonitric mixtures may be used to prepare cellulose trinitrate (32a, b, 49a, d, 105), but

Bennett and Timell (32a) found that this reagent converted only highly-purified cellulose to the undegraded trinitrate. This fact precluded its use as a nitrating agent for a rigorous study of the structure of wood and its components. Treatment of whole wood with acetonitric mixtures leads to products which are only slightly soluble in organic solvents (54b, 134, 136) or brings about the decomposition of the protolignin (137, 336, 383a). The poor solubility properties of the nitrated wood obtained by means of acetonitric mixtures may be connected with the poor swelling ability of this reagent (32a).

Use of phosphonitric mixtures is attended by similar disadvantages. These reagents do not allow the preparation of cellulose trinitrate (32a, 379) and therefore, presumably, would also not give complete nitration of the carbohydrate components of wood. The bulk of evidence presently available indicates that phosphonitric mixtures bring about the nitration of cellulose without degradation (174, 369). Although solubility properties of the products from long treatment of wood with this reagent are satisfactory (amounting to ninety percent or more in many cases), this is brought about at the expense of the protolignin, which is almost entirely destroyed (5, 60b, 62, 292a), 365a, b, c, 377b, c, d). Thus, the product of the reaction of phosphonitric mixtures with wood is nitrated carbohydrate material rather than nitrated wood.

Both aceto- and phosphonitric mixtures are, of course, liquid reagents, so that the possibility of loss of at least a small amount of the product to solution is always present. This is borne out by the isolation of nitrated lignin and lignin decomposition products

from the reaction mixtures (137, 292a, 336, 383a), the coloring of the solution during reaction (377e), etc.

This brief recapitulation of some of the data given in the historical survey will show that, although useful information concerning some of the components of wood has been gained from a study of these nitration products, the study of whole wood through nitration technics has not yet been possible. It was the goal of the present research to develop a technic which would convert all of a wood sample into a completely nitrated product without solution losses while avoiding oxidation and hydrolytic decomposition of the wood components.

It was considered that the use of a nitrating reagent more powerful than any used hitherto might result in more highly-substituted products which, in turn, might have better solubility properties. There was an additional reason, also, for the desire to reach limit nitration, for it has been found that only completely substituted cellulose derivatives can be fractionated according to their molecular weights without the simultaneous fractionation according to different degrees of substitution (1c, 32b, 377c). It was also considered that the use of a gaseous nitrating agent would preclude loss of material to a solution medium, so that the whole nitrated product would be available for study. Such a reagent would not, of course, preclude the possibility of loss of gaseous material formed during the reaction.

The nitronium ion is listed (148) as being the most powerful nitrating agent known. It has recently been shown that C-nitration (of aromatic nuclei) (213), N-nitration (43) and O-nitration (43, 216,

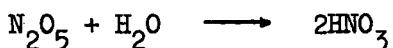
235) all occur through attack by the nitronium ion. One excellent source of nitronium ions is dinitrogen pentoxide which, in the solid state, exists as nitronium nitrate ( $\text{NO}_2^+\text{NO}_3^-$ ) (161). In the gaseous state, the covalent form prevails (323). Interconversion between the two forms occurs very readily. Therefore, it was considered probable that, in the presence of highly polar hydroxyl groups, nitronium ions would be freely available from gaseous dinitrogen pentoxide, and that, therefore, the reagent should be a powerful reagent for the nitration of whole wood. Furthermore, since dinitrogen pentoxide is a polar gas, it was expected to be a good swelling agent for wood (406b) and the linear structure of the nitronium ion (94, 159, 161, 215) would ensure its penetration into the woody structure.

There is no lack of experimental proof to attest that gaseous dinitrogen pentoxide is, indeed, a powerful nitration agent. Cellulose trinitrate has been prepared by use of this reagent (98, 272a, c, 387) in reaction times as short as twenty minutes. Rapid nitration, leading to products with high degrees of substitution have also been reported in its reactions with pectins (393) and starch (387). A variety of non-carbohydrate compounds, including those with aromatic nuclei have also been nitrated by gaseous dinitrogen pentoxide (23, 142a, b).

Previous work (328a, b, 190) had shown that use of gaseous nitryl halides as nitrating agents is limited to reaction with more reactive compounds, and that the reaction is not uniquely nitration.

Use of dinitrogen pentoxide as the nitrating agent offered

another very attractive feature; Vollmert (393) recently showed that its reaction with pectins occurred in a polymer-analogous manner (i.e., without degradation of carbohydrate chains). This was probably due, in part, to the fact that water of reaction would have a very short existence as such, but would be converted immediately to nitric acid



thus ensuring that the reaction medium remained anhydrous.

Only one possible disadvantage to the use of dinitrogen pentoxide was known. It has been shown that it is a strong oxidizing agent (293). However, it was hoped that its power to cause rapid and complete nitration of carbohydrate and other material would ensure that this was the dominant, if not the only, reaction.

Relatively pure dinitrogen pentoxide is readily prepared by treatment of nitrous acid-free, anhydrous nitric acid with phosphorus pentoxide (146, 153, 306), and convenient technics for handling the compound have been worked out by Vollmert (393) and others.

### 3. THE SCOPE OF THE EXPERIMENTAL WORK

A rather comprehensive series of preliminary experiments was carried out with four objectives in mind: (1) to test the efficiency of the apparatus and (2) the method of preparation of dinitrogen pentoxide; (3) to establish optimum reaction conditions, and (4) to further determine the scope and limitations of gaseous dinitrogen pentoxide as a nitrating agent. Mannitol was chosen as the reference compound to accomplish (1), (2) and (3), both because its hexanitrate

was a known and well-characterized compound and because it seemed to be a suitable model for cellulose, which contains long chains of secondary alcohol groups and few, if any, free reducing groups. In order to determine more of the scope and limitations of the nitrating effect of gaseous dinitrogen pentoxide, its reaction with a number of other simple carbohydrate substances, and some compounds containing aromatic nuclei, was studied. The reaction with isolated wood components was also tested.

These preliminary studies were followed by the nitration of extractive-free western red cedar heartwood. Early work was concerned with the establishment of reaction conditions such that maximum uptake of nitrogen would occur, accompanied by a minimum of side reactions. Work on determining the properties of the nitrated wood was also initiated, with special emphasis on the solubility in organic solvents.

#### 4. THE APPARATUS

The apparatus has been described and illustrated in Section I, Plates I, II and III. With one minor exception, it was found to be suitable for the work described here. It was found that the inlet tube of Flask J (Plate II) often became plugged with solid dinitrogen dioxide, and it is therefore recommended that a tube with bore larger than eight millimeters be used.

All joints were lubricated with Apiezon M high vacuum grease, which was not appreciably attacked by nitric acid vapors, gaseous dinitrogen pentoxide or ozone. This grease also maintained a suitable

degree of plasticity at the low temperatures involved in some of the steps of the reaction.

#### B. PRELIMINARY EXPERIMENTS

##### 1. THE NITRATION OF D-MANNITOL: ESTABLISHMENT OF OPTIMUM EXPERIMENTAL CONDITIONS

Results of the nitration of mannitol are shown in Table XXIV. The products listed in each set were obtained under different experimental conditions.

I. The reagent used was second-run material, i.e., dinitrogen pentoxide which was excess from a previous nitration. It had been prepared under the conditions described for Set II.

II. The dinitrogen pentoxide used was freshly prepared from anhydrous nitric acid (ten millilitres or less) in the reaction assembly (Plate III) immediately before use. In the experiments reported in Sets I and II, the mannitol was weighed directly into the reaction flask, and at the end of the reaction, the product was removed from the reaction flask by quantitative transfer of its solution in ethanol.

III. The dinitrogen pentoxide used was first-run reagent which had been prepared (in the apparatus shown in Plate II) from ten millilitres of nitric acid, in the presence of ozone. The mannitol was weighed into tared vials so that the crude product could be directly weighed without first being dissolved in ethanol.

IV. Experimental conditions were the same as described for Set III, except that the dinitrogen pentoxide was prepared from fifteen millilitres of nitric acid.

TABLE XXIV

The Nitration of D-Mannitol with Dinitrogen Pentoxide

Set	Weight of Mannitol Used (Mg.)	Reaction Time (Hr.)	% Yield	Melting Point (Corrected) (a)	$[\alpha]_D$ (a,b)
I	81.4	3	33.6	syrup	12.3
	55.1	5	98.2	107.5 - 108	49.3
	77.9	5.75	87.0	93 - 101	54.6
	139.9	13	73.5	90.5 - 99	(c)
II	55.9	2	101.5	107 - 107.5	(b)
	74.5	4	101.0	108 - 109	47.6
	51.7	5	101.7	109 - 110.5	53.5
	48.1	8	102.0	108 - 108.5	76.6
	141.9	10	89.5	105 - 106	72.3
	398.1	12	60.0	-	-
	230.0	13.5	90.1	111 - 111.5	43.3
III	44.1	1	57.8	85 - 98	-
	52.3	2	100.0	111 - 111.5	19
	63.4	2	100.0	109.5 - 110.5	70.7
	55.5	4	99.8	107 - 110	64.0
IV	59.5	2	99.0	106.5 - 108	40.5
	40.5	3.5	99.0	106 - 107	14.7
	60.7	6	98.7	105.5 - 107.5	34.4

- a. The reported constants for pure D-mannitol hexanitrate are shown in Table XXV.
- b. All rotations were taken using ethyl alcohol as solvent.
- c. The optical rotation changed with time.

From an examination of the results shown in Table XXIV a number of generalizations concerning optimum experimental conditions could be made:

The size of the sample which could be handled successfully was definitely limited. This probably resulted from lack of penetration of the nitrating gas into the finely-divided crystalline mannitol which was used as starting material, and was a function of the apparatus rather than of the method.

Comparison of the results in Sets I and II indicated that the crude products were obtained in greater yield and in a state of greater purity when freshly-prepared dinitrogen pentoxide was used. This was indicated even more clearly by the products of the two five-hour reactions, which were prepared under conditions as closely identical as possible. The reaction was also much more reproducible when freshly-prepared dinitrogen pentoxide was used. These results differed from those of Vollmert (393) who reported that dinitrogen pentoxide excess from a previous reaction was satisfactory for the preparation of pectin, pectic acid, starch and cellulose nitrates.

Although the yields and melting points of the products were generally satisfactory in Sets I and II, the high specific rotations indicated that side reactions were probably occurring. Since it was known that dinitrogen pentoxide readily decomposes to dinitrogen tetroxide and oxygen (138, 222) (through the dinitrogen trioxide), both of which are oxidizing agents, it was thought desirable to prepare the reagent in the presence of ozone which not only inhibits this decomposition, but also converts dinitrogen tetroxide to dinitrogen pentoxide (375).

When dinitrogen pentoxide was prepared in the presence of ozone (Set III), the yields and melting points of the samples of D-mannitol hexanitrate were more satisfactory. This, at first, may not be evident from Table XXIV. However, when it is considered that the products listed in Set III were the actual crude products, not treated with warm ethanol (which would, no doubt, lead to a certain amount of purification by leaving behind insoluble material such as relatively unsubstituted mannitol) the results are more striking. The high specific rotations, however, were still disturbing.

Since a survey of the literature showed that the nitrating agents were always used in large excess, the next modification in procedure was to prepare the dinitrogen pentoxide from a larger amount (fifteen millilitres) of anhydrous nitric acid. Results in Set IV showed that, under these conditions, the reaction was almost entirely reproducible and the specific rotation was more uniform. The suggested presence of unreacted mannitol was in agreement with the melting point and specific rotation of D-mannitol (Table XXV).

Later work brought out one additional experimental detail, which may be mentioned here. For the simple model substances studied, better products were obtained when the dinitrogen pentoxide was freeze-distilled into the reaction flask before the reaction was allowed to proceed. With wood, cellulose and xylan, the presence of solid dinitrogen pentoxide in the reaction flask prior to starting the reaction seemed to make little difference in the character of the product obtained.

In summary, it may be seen that nitration occurred very rapidly

TABLE XXV

Physical Constants of D-Mannitol and Its Nitrate Derivatives  
(182)

Compound	m.p.	$[\alpha]$ <sub>D</sub>
Mannitol	166-167	-0.53 (a)
Mannitol pentanitrate-1,2,4,5,6	81-82	43.6 (b)
Mannitol hexanitrate	111-112	43.1 (b)

a. In water.

b. In ethanol.

and, for mannitol, showed no optimum time within the range of two to eight hours. It also showed that mannitol hexanitrate was stable under the conditions used. On the basis of these results, attention was next turned to the nitration of other model substances, carbohydrate polymers and wood.

## 2. THE NITRATION OF SIMPLE CARBOHYDRATE COMPOUNDS

As already mentioned, the small amounts of material which could be nitrated at one time imposed a definite limitation on the nitration technic. However, this was partially overcome by using several small vials (up to six) in the same reaction flask at the same time. The results of these nitrations are reported in Tables XXVI, XXVII and XXVIII. The set numbers I, II ... have the same significance as recorded for Table XXIV.

Yields were calculated as the ratio of weight of crude product to the theoretical yield. The initial yield was based on the weight of the product at the end of the reaction. It was found that all products lost a certain amount of weight on standing (desorption of nitric acid and/or dinitrogen pentoxide?), and they were therefore stored in a vacuum desiccator over phosphorus pentoxide and solid potassium hydroxide until the weight became constant. It was on this constant weight that the "final" yield was based.

It was of interest to note that this weight loss bore a direct relationship to the degree of nitration of the product. Samples whose weight increase was close to the theoretical generally lost very little weight and attained constancy after storage for two or three days. Samples whose weight increase was significantly less than the theoretical suffered large weight losses and required a week or more of storage in vacuo to come to constant weight. This, presumably, was due to the presence of polar centres (unsubstituted hydroxyl groups) which more firmly held the nitric acid of reaction and/or oxides of nitrogen.

All melting points reported in Tables XXVI, XXVII and XXVIII were corrected. For comparison, the physical constants for the pure nitrate derivatives are shown in Table XXIX.

The results of the nitration of sorbitol and dulcitol, shown in Table XXVI, were somewhat surprising. Most unexpected were the poor results in the formation of dulcitol hexanitrate, which is readily prepared by use of sulfonitric mixtures (279, 401). In no instance in the present work was anything even approaching a quantitative

TABLE XXVI

The Nitration of Sugar Alcohols  
with Dinitrogen Pentoxide

Alcohol	Sample Wt. (Mg.)	Reaction Time (Hr.)	% Yield		Melting Point	Nature of Product (a)
			Initial	Final		
Dulcitol						
	II 312.9	16	79.5	-	99-103.5	S(g)
	IV 64.10	1-1/2	66.65	62.50	-	S(w)
	54.50	1-1/2	96.15	(b)	-	Sy + C
	60.30	1-2/3	69.80	64.86	92-122	S(w)
Mannitol	39.90	3	82.65	76.03	93-105	S(y)
	48.65	6	93.78	84.05	94.5-97.5	C(g) + Sy
Sorbitol	IV 17.90	3	100.00	99.93	109.5-110.5	C(w)
	16.10	3	101.3	100.8	107-107.5	C(w) (c)
Sorbitol	II 303.3	16	-	-	-	Sy
	IV 60.40	1-1/4	98.13	93.86	44-47	Sy → C
	71.95	1-1/2	98.82			Sy(g)
	98.60	1-1/2	97.83			Sy(g)
	53.10	1-1/2	101.36	(b)	-	C
	102.65	1-1/2	101.25	(b)	-	C
	37.15	1-2/3	98.41	92.44	-	C
	66.10	1-2/3	96.82	92.07	-	Sy + C
	47.10	3	97.35	89.22	-	Sy + S →
	79.40	6	98.47	92.64	-	Sy + C Sy → C

a. The symbols used have the following significance: S = amorphous solid; Sy = syrup; C = crystalline product; g = green; w = colorless.

b. Partial decomposition of the product occurred during later treatment.

c. The specific rotation of the product, measured in ethanol, was 24.2°.

yield obtained. The products also were poor in appearance, being amorphous and often having a faint blue tinge. In all cases, there was evidence that liquid had been present in the reaction vial at some time during the reaction, although it was not observed.

The two results for mannitol are included here for reference purposes; they were obtained during the same series of reactions as the other compounds reported in Set IV. The products were colorless and crystalline, in contrast to those of the dulcitol hexanitrate preparation. In some instances, crystals of mannitol hexanitrate were found growing from the surface of the product. At no time was liquid noticed in preparations of mannitol hexanitrate, and there was no indication that liquid had been present at any time during the reaction. This was the only such case amongst all the simple carbohydrate compounds nitrated.

Results from the nitration experiments on sorbitol were also unexpected in view of the reported difficulties in preparing crystalline sorbitol hexanitrate by use of more conventional nitrating mixtures.

It was only recently that the hexanitrate was obtained in crystalline form (376, 388). Tettamanzi and Arnaldi (376) were able to obtain the hexanitrate in ninety-seven percent yield by nitration at -15° C. in a mixture of fuming nitric and concentrated sulfuric acids. However, Urbanski and Kwiatkowska (388) found that nitration at temperatures lower than -10° C. gave mainly a syrup which analyzed for sorbitol pentanitrate, and that only when the temperature was above 0° (best at 3-5° C.) was the hexanitrate the main product (eighty percent yield).

In the present work, the products, at the end of the reaction period, were mobile liquids, which became more viscous or crystallized during the evacuation of the reaction system before opening to the atmosphere. One set of crystals (from the ninety-minute runs) were very large, translucent, white needles. Unfortunately, the crystals were lost by decomposition when the product was inadvertently subjected to heat, and before either constant weight or melting point determinations could be carried out. The products of the hundred-minute runs were also crystalline, although the crystals were much smaller. No melting point was determined, as the product was quite "gummy." It should be mentioned that, for sorbitol, the relative yields were probably of more importance than the absolute yields. The starting material was hydrated sorbitol which had been stored in a desiccator for three years, so that its state of hydration at the time of reaction was not known.

Nitration of D-fructose and D-mannose gave unsatisfactory results. The yields were low and the products syrups (Table XXVII). Since neither of these compounds was an analogue of those expected in wood, their reaction with dinitrogen pentoxide was not studied in detail. However, it should be mentioned that both fructose and mannose have been converted to their nitrates by treatment with mixtures of concentrated nitric and sulfuric acids (402). Mannose was reported to be converted to the pentanitrate, but no yields were given; mannose pentanitrate was not stable, and lost forty-six percent of its weight on standing at 50° C. for twenty-four hours.

Fructose did not behave as well as mannose in the nitrating

TABLE XXVII  
The Nitration of Monosaccharides

Compound	Sample Weight (Mg.)	Reaction Time (Hr.)	% Yield		$[\alpha]_D^T$	Nature of Product (a)
			Initial	Final		
D-Fructose						
IV	60.30	1-1/4	88.05	69.29	-	Sy(w)
	148.05	2	61.40	49.83	-	Sy
D-Mannose						
II	168.8	3-1/2	69	-	+16.6	Sy
	163.0	21	91.5	-	+56	Sy
$\alpha$ -Methyl-D-Glucoside						
II	425.8	2	86.9	-	101	Sy
	155.1	4	(b)	-	-	Sy
$\beta$ -Methyl-D-Glucoside						
II	225.5	4-1/2	65.2	-	-0.88	Sy + S
IV	88.90	1	74.63	67.56	-	Sy + C
	54.00	1-1/2	102.5	(b)	-	Sy + C
	60.15	1-1/2	104.0	70.33	-	C
	52.20	1-2/3	99.41	88.66	-	Sy → C
	43.60	3	(c)	(d)	-	
	28.20	3	71.6	65.41	-	Sy
	35.30	6	96.06	94.23	-	Sy(g) + C → C
				82.37	-	Sy + C
(f)						

(a) Sy = syrup, S = amorphous solid, C = crystalline product, w = colorless, g = green.

(b) Partial decomposition of the product occurred during later treatment.

(c) Product was lost from the reaction tube during evacuation, so that results were not quantitative.

(d) Corrected m.p. 103-111° C.

(e) Corrected m.p. 112-113° C.

(f) Corrected m.p. 94-111° C.

mixture (402). The product separated from the reaction mixture as a dark yellow oil which became more colored on standing. Yields were low (no quantitative data are given). Although the oil became "solid" when poured into ice water, it again became a syrup when allowed to warm to room temperature. By fractionation with alcohol, two crystal forms were isolated. Analyses for carbon, hydrogen and nitrogen suggested that the compounds were not the expected fructose pentanitrates, but rather, trinitrates of a fructose anhydride. Small amounts of syrup analyzing for fructose pentanitrate were isolated from the mother liquors. Therefore, it was suggested that fructose pentanitrate first formed and then decomposed under the nitrating conditions. Melting points and optical rotations of the crystalline compounds obtained by Will and Lenze (402) are reported in Table XXIX.

Studies of the nitration of the methyl glucosides were concentrated on the  $\beta$ -anomer, both because of its availability in this laboratory, and also because of its closer relationship to cellulose, which also has the  $\beta$ -glucosidic linkage. Results of the nitration of  $\alpha$ -methyl-D-glucoside are shown in Table XXVII only for comparison. The behaviour of the nitration product of  $\beta$ -methyl-D-glucoside was similar in all cases where crystallization occurred. The reaction mixture, at the end of the reaction time, was a mobile liquid which, during evacuation of the system prior to opening, suddenly "erupted" (often causing product to be lost from the vial) and became either much more viscous or crystalline. The crystals generally were not large, due to their speed of formation. Unfortunately, the reaction was

not as reproducible as could have been wished and, although excellent results were obtained in some cases, yields and melting points varied. Results of the present nitration of both the  $\alpha$ - and  $\beta$ -anomers were very disappointing, in view of the ready preparation of the tetranitrates in yields of up to ninety-nine percent (53b), by use of acetonitric mixtures.

Attempts to prepare the crystalline octanitrates of four disaccharides by use of gaseous dinitrogen pentoxide were not successful. Most interest was attached to the reaction of cellobiose, because of its close relationship to cellulose. In only one case was a crystalline product obtained (reported in Set IV, Table XXVIII), where a single rosette of needles was found embedded in the surrounding clear syrup. (It is most unfortunate that these were lost soon after preparation, so that it is not known whether or not the entire product might have crystallized on standing.) Attempts to duplicate the production of crystals were not successful. In the other preparations, the product was a syrup which set to an iridescent froth during the evacuation process. Attempts to recrystallize the combined products from Set V reactions by the method of Ashford, Evans and Hibbert (12) were not successful.

Results of the attempted nitrations of lactose, maltose and sucrose were equally disappointing. No crystals were obtained, the products of all reactions being clear syrups which became froths during the evacuation step. Melting points of some of these hard froths are shown in Table XXVIII. No crystals were obtained in attempts to recrystallize the syrups.

TABLE XXVIII

The Nitration of Disaccharides

Compounds	Sample Weight (Mg.)	Reaction Time (Hr.)	% Yield		Melting Point	$[\alpha]_D^T$	Nature of Product
			Initial	Final			
Cellobiose							
II	188.3	4	81.5	-	-	24.1	Sy
	224.2	11-1/2	69.0	-	-	14.6	Sy(g)
V (b)	98.3	1-1/3	98.3	90.3	-	31.8	Sy(g) + S
	74.6	1-3/4	86.3	-	-	61.1	Sy + S
	137.2	2	97.5	-	-	-	Sy + S
	74.2	2-1/3	101	93.0	-	46.8	Sy(g)
	90.4	3	89.8	73.6	-	24.7	Sy(c)
	64.0	4	102	96.5	-	53.1	Sy(c → g)
	228.0	4-1/2	96.8	85.6	-	-	Sy + S
IV	45.55	1	93.44	69.18	125-175(d)	-	Sy
	38.10	1-1/2	96.15	(a)	-	-	Sy + C
	84.88	1-1/2	84.88	59.61	-	-	Sy(y)
	44.85	1-2/3	86.85	73.43	88-106	-	Sy(y)
	39.00	2	106.9	71.67	125-170(d)	-	Sy
	47.60	3	96.71	74.03	-	-	Sy(c)
Lactose							
IV	109.00	1	60.98	57.41	151-170(d)	-	Sy + S
	191.40	2	80.11	65.58	146-170(d)	-	Sy
	81.50	6	103.6	74.51	-	-	Sy
Maltose							
IV	66.35	1	78.42	67.70	-	-	Sy
	45.20	1-1/2	100.7	(a)	-	-	Sy
	75.15	1-1/2	79.52	64.03	-	-	Sy
	24.80	1-2/3	98.88	87.61	84-97	-	Sy
	53.30	2	102.6	83.78	-	-	Sy(g)
	37.15	6	97.56	72.85	-	-	Sy
Sucrose							
IV	153.60	1	56.01	54.63	-	-	Sy(w)
	121.85	2	62.52	58.76	-	-	Sy
	80.65	3	54.00	53.58	-	-	Glass
	53.90	3	74.48	68.95	-	-	Sy(c)
	54.05	6	63.70	60.55	-	-	Sy

(a) Partial decomposition of the product occurred during later treatment.

(b) The reaction conditions are identical to those of Set IV, except that the reaction was allowed to proceed for twenty to thirty minutes at room temperature, before the temperature was lowered to  $1 \pm 2^\circ$ .

The octanitrates of cellobiose, lactose, maltose and sucrose are reported in the literature. Will and Lenze (402) were unable to prepare crystalline sucrose octanitrate (by use of sulfonitric mixtures); although a syrupy form was readily obtained. The crystalline form has been reported by other workers (201, 246a). It has been suggested (295) that the presence of nitrous oxides is detrimental to the preparation of sucrose octanitrate.

Lactose has been reported to nitrate very well in sulfonitric mixtures (402) and was the only one of the compounds nitrated by Will and Lenze to precipitate as a solid from the reaction mixture. The yield of crude product was ninety-five percent. Lactose octanitrate was found to be unstable; the weight loss at 50° C. was 0.7% in eight days and 40% in forty days.

Maltose octanitrate is readily prepared in good yield by treatment of maltose with sulfonitric mixtures (12, 402). A product which analyzed for 15.5% nitrogen (maltose octanitrate requires a nitrogen content of 15.95% nitrogen) has been prepared by use of a mixture of chloroform, sodium fluoride and dinitrogen pentoxide (70).

Cellobiose octanitrate has also been readily prepared in good yield by use of both sulfonitric (12) and acetonitric (127a) mixtures. It has been found (127) to be a particularly unstable compound.

Since the purpose of the present work on the nitration of simple carbohydrate molecules was only to determine which compounds would react well with dinitrogen pentoxide, no detailed investigation of the products of reaction was carried out. On the whole, results were disappointing. However, the following conclusions can be drawn from the work reported here.

TABLE XXIX  
Physical Constants of the Nitrate Derivatives  
of Some Carbohydrate Compounds

Compound	Melting Point	[ $\alpha$ ]	Ref.
D-Dulcitol hexanitrate	94-95, 98-99	0	27, 279
D-Sorbitol hexanitrate	54, 54.5-55	-	35, 376, 388
D-Fructose (anhydride) trinitrate	137-139, 48-52	62 (a) 20 (a)	402
D-Mannose pentanitrate	81-82	93.3 (a)	246a, 402
$\alpha$ -Methyl-D-glucoside tetranitrate	46 to 50 (e)	146 (c) 136-140 (a)	53b, 206a, 402
$\beta$ -Methyl-D-glucoside tetranitrate	116 to 119 (e)	9.25 to 11.5	53b, 206a, 246a
Cellobiose octanitrate	140, 154-155	-	12, 127a, 401
Lactose octanitrate	145-146	74.2 (a)	402
Maltose octanitrate	163-164 (d)	128.6 (b)	12, 402
Sucrose octanitrate	85-86	56.66 (a) 55.9 (c)	201, 246a

(a) In alcohol.

(b) In acetic acid.

(c) In chloroform.

(d) Melted with decomposition.

(e) Reported melting points are in the range given.

(1) In agreement with the literature, it has been found that nitration occurs very quickly, in the presence of gaseous dinitrogen pentoxide.

(2) Gaseous dinitrogen pentoxide seemed not to be universally useful for the preparation of the nitrates of simple carbohydrate molecules. It was felt that the poor results with most of the compounds studied were not entirely due to the lack of establishment of optimum reaction conditions, since a variety of reaction times was used, but seemed to be dependent on the nature of the starting material in a way which was unpredictable and uncorrelated with the structure of the compound. This was shown most clearly in the divergent results for the nitration of dulcitol, mannitol and sorbitol, and was reflected also in the crude products obtained from the nitration reactions with lactose, maltose and cellobiose. These three compounds differ from sucrose in having free reducing groups but, since results were poor in all four cases, they cannot be attributed solely to oxidation reactions. Neither were the poor results explicable on the basis of hydrolyses of the glycosidic linkage, since  $\beta$ -methyl-D-glucoside gave products of fairly satisfactory yield and purity. Therefore, it seems safe to say that dinitrogen pentoxide does not differ from the more common nitrating agents, since similar variations in reaction have been noted for maltose and lactose (402) and for cellobiose and maltose (12), on which parallel nitration reactions have been carried out. However, it must be concluded that conventional nitrating mixtures seem to be much more useful than gaseous dinitrogen pentoxide in the preparation of nitrates of simple carbohydrate compounds.

(3) It was possible that the decrease in weight between the initial and final determinations may not have been caused entirely by loss of adsorbed nitric acid or dinitrogen pentoxide. Instability is a property common to all organic nitrates, in greater or lesser degree (127), so that the final yields probably reflect loss of weight both because of desorption of gas and decomposition of the products.

(4) In no case was there a noticeable trend in the yield in relation to the time of reaction. This indicated that all the nitrates prepared were stable under the reaction conditions employed.

(5) The results presented show that the reaction, as carried out in this work, was not entirely reproducible, except in the case of mannitol. Since reaction conditions were held as constant as possible, it must be concluded that some unknown factor was operating. This, naturally, imposed a limitation on the method as described here.

(6) Since the results with mannitol were excellent, on the whole, and since this substance was considered to be a reasonable model compound for cellulose (and other polymeric carbohydrate substances), it was felt that further study of the reaction of dinitrogen pentoxide with carbohydrate polymers and wood was justified.

### 3. THE NITRATION OF NON-CARBOHYDRATE MODEL COMPOUNDS

It was hoped that the model substances chosen would show the efficiency of dinitrogen pentoxide in nitrating the substituted aromatic nucleus (as may be found in protolignin) and also indicate possible degradation effects such as oxidation, demethylation and the

substitution of carbonyl by nitro groups. As with the simple carbohydrate compounds, the object of the work was to determine which nitrations, with gaseous dinitrogen pentoxide, occurred in a manner suitable for synthetic purposes. Therefore, no attempt was made to study the resultant products, except, in the light of results reported in the literature, to make some inference as to the possible course of reaction.

Tartaric acid dinitrate was prepared in one hundred percent yield, by treatment of tartaric acid with gaseous dinitrogen pentoxide (Table XXX). This compound had previously been prepared in a similar manner by Gibson (142a), who obtained a yield of eighty-one percent, and by Krauz and Majrick (244a), by exposure of tartaric acid to "oxides of nitrogen." In both instances, tartaric acid dinitrate was found to be unstable in moist air, and to decompose on melting.

Benzoic acid was likewise smoothly and completely nitrated by gaseous dinitrogen pentoxide. The melting points of the finely crystalline, slightly yellow, crude products and the yields of over one hundred percent (Table XXX) indicated that disubstitution may have occurred to a very slight extent. The melting point of one of the preparations, after recrystallization from ethanol-water, showed that the expected meta isomer had been prepared. These results were the more interesting in view of the fact that Haines and Adkins (170) reported that benzoic acid was completely resistant to nitration by a mixture of dinitrogen pentoxide in carbon tetrachloride, and Cooper and Ingold (92) obtained only an eighty percent

TABLE XXX

The Nitration of Non-Carbohydrate Model Compounds  
with Dinitrogen Pentoxide

Compound	Weight Sample (Mg.)	Reaction Time (Hr.)	% Yield		Melting Point (crude)	Nature of Product (a)
			Initial	Final		
Tartaric Acid IV	118.25	4	100.00	100.00	-	
Benzoic Acid IV	59.85	1-3/4	106.1(b)	101.5	122-133	Sy - S
	67.55	3	104.3(b)	101.3	129.5- 131.5(e)	
Mandelic Acid IV	107.70	6	103.18(b)	100.6	117-128	Sy - S
Salicylic Acid IV	72.40	1-3/4	107.6(c)	97.57	99-106(f)	Sy + S → C
	49.95	1-3/4	100.6(b)	(d)	gum	Sy (g)
	34.30	3	100.6(b)	(d)	80-90	Sy (g) → S
Vanilllic Acid IV	41.30	1-3/4	97.51(b)	(d)	80-113(d)	Sy → gum
	33.55	6	73.47	(d)	gum	Sy → gum
Vanillin II	(g)					
IV	62.15	1-3/4	119.8(b)	(d)	-	Sy → gum
	39.00	4	84.38	(d)	gum	

(a) Sy = syrup, S = amorphous solid, C = crystalline product.

(b) Calculated on the basis of a mononitro compound.

(c) Calculated on the basis of a dinitrocompound.

(d) Weight loss was steady and continuous, so that no final yields could be calculated.

(e) The product recrystallized from ethanol-water melted at 135-136° C.

(f) The product recrystallized from ethanol-water melted at 214-218° C. with decomposition.

(g) Two runs were attempted. In both cases, rapid decomposition of the vanillin occurred immediately upon contact with the vapors of dinitrogen pentoxide.

yield by use of a mixture of dinitrogen pentoxide, phosphorus pentoxide and carbon tetrachloride.

Only one attempt was made to nitrate mandelic acid. The final yield of crude, crystalline product was 95.6%, based on the weight increase expected for formation of a disubstituted compound. The melting point of the crude product was 99-106° C. Recrystallization from ethanol-water yielded a yellow-tan crystalline powder, which melted at 214-218° C., with decomposition. This high melting point was quite unexpected in view of the melting point of the crude product. No explanation for this behaviour has been found, except to suggest that a hydrate or alcoholate was formed. Since the weight increase corresponded closely to that of a disubstituted compound, it was assumed that the expected nitrate ester of nitromandelic acid had been formed. This compound has not previously been reported in the literature. The only other alternative, to correspond to the weight increase, would be that one of the dinitrophenylglyoxalic acids was formed. (This would involve oxidation of the secondary alcohol, followed by dinitration of the ring.) This, however, was unlikely, in view of the results with benzoic acid which suggested that the presence of meta-directing groups tend to favor mono substitution even by so powerful a nitrating reagent as dinitrogen pentoxide. Neither weight increase nor melting points corresponded to those for any of the monosubstituted mandelic or phenylglyoxalic acids reported in the literature (Table XXXI).

Attempts to prepare a nitrated salicylic acid were unsuccessful. The products were yellow-green syrups which did not crystallize.

TABLE XXXI

Physical Constants of Non-Carbohydrate Model Compounds

Compound	Reported m.p. (°C.)	Ref.
Tartaric acid dinitrate	decomp. at 40° (1)	342
<u>o</u> -Nitrobenzoic acid	146-147	185a
<u>m</u> -Nitrobenzoic acid	140-141	"
<u>p</u> -Nitrobenzoic acid	238	"
<u>o</u> -Nitromandelic acid (racemate)	140	185b
<u>m</u> -Nitromandelic acid ( " )	119-120	"
<u>p</u> -Nitromandelic acid ( " )	126-127	"
<u>o</u> -Nitrophenylglyoxalic acid	46-47 (2)	28a
<u>m</u> -Nitrophenylglyoxalic acid	122-23, 156-157 (3) 77-78, 105	28a, 18
<u>p</u> -Nitrophenylglyoxalic acid	150	18
3-Nitrosalicylic acid	148-149	185c
4-Nitrosalicylic acid	226, 235, 229	185c, 370
5-Nitrosalicylic acid	229-230	"
6-Nitrosalicylic acid	179-180	"
2-Nitrovanillic acid	210	286
5-Nitrovanillic acid	214-215	318
3,5-Dinitrovanillic acid	215	28c

(1) Unstable in moist air.

(2) This is the melting point of the hydrate.

(3) This is the melting point of the anhydrate.

On storage in vacuo, over phosphorus pentoxide and solid potassium hydroxide, there was continued weight loss, so that no final yield could be calculated. Since this effect was not noticed with tartric acid dinitrate, nitrobenzoic acid or the nitrated mandelic acid, it seemed reasonable to attribute this behaviour to the presence of the phenolic hydroxyl group. It might be expected that salicylic acid would react in a manner analogous to that described below for vanillin and vanillic acid, i.e., nitration accompanied by decarboxylation or decarbonylation. Traynard and Robert (383c) found that p-hydroxybenzoic acid was decarboxylated in dilute solutions of nitric acid in acetic acid. Francis (129), however, reported no such effect on treatment of salicylaldehyde with benzoyl nitrate; the main reaction was one of oxidation.

In the present work, vanillic acid and vanillin also yielded nitration products which did not come to constant weight on standing (Table XXX). Results with vanillic acid were particularly poor and, in one instance, the weight of product was lowered to less than the weight of vanillic acid used originally, while loss of weight still continued. Such results were not entirely unexpected, since it was known that both vanillin (34, 284) and vanillic acid (318a) were converted to dinitroguaiaacol by treatment with nitric acid. 5-Nitrovanillin has been prepared by treatment of vanillin with benzoyl nitrate (129), and by treatment with the oxides evolved from a mixture of sodium nitrite and sulfuric acid (275, 364); the reported yields, however, were not quantitative. Traynard and Robert (383c) have recently carried out a detailed study of the reaction of

vanillin and vanillic acid with fuming nitric acid in acetic acid, and showed that vanillic acid was very readily decarboxylated. The products of this reaction were 5-nitrovanillic acid (in small yield only) and dinitroguaiaacol. On the other hand, vanillin was converted to 5-nitrovanillin in yield of eighty percent, using this same reagent. Gustaffson and Andersen (164) found that similar results were obtained when solutions of nitric acid and sodium nitrite in ether were used. Both vanillic acid and 5-nitrovanillic acid were converted to 2,4-dinitroguaiaacol in yields of approximately sixty percent. Vanillin and 5-nitrovanillin were converted to dinitroguaiaacol only to the extent of twelve and nine percent, respectively. The presence of oxides of nitrogen enhanced the decomposition of vanillin, vanillic acid and related compounds (164). This would readily explain the reaction, reported in Table XXX, in which vanillin was treated with dinitrogen pentoxide which had not been prepared in the presence of ozone. Destruction of vanillin began immediately upon contact with this impure dinitrogen pentoxide. The effect was not noted in the reactions with dinitrogen pentoxide which had been prepared in the presence of ozone. The ready reaction with oxides of nitrogen would also explain the continuing weight loss of both products on storage, since oxides of nitrogen seemed always to be present in the desiccator in which the preparations were stored.

Although Gustaffson and Andersen (164) found that little, if any, demethylation of either vanillin or vanillic acid occurred during nitration, demethylation has been reported many times to occur

in reactions of phenolic ethers (64), and of protolignin and lignins with various nitric acid mixtures (see the sections on acetonitric mixtures and on the nitration of lignin, in the historical survey).

In summary, it may be said that dinitrogen pentoxide caused rapid and complete nitration of compounds where oxidative degradation was inhibited, e.g., with benzoic and tartaric acids. The reaction with mandelic acid led to no definite conclusion since many of the possible products have not been reported in the literature. With salicylic acid, vanillic acid and vanillin, it seemed that gaseous dinitrogen pentoxide differed little from the more conventional nitrating mixtures in its power to cause decarboxylation and decarbonylation. In fact, the pentoxide may have enhanced powers for causing decarboxylation in view of the results obtained with salicylic acid, which may be successfully nitrated by other reagents.

### C. THE NITRATION OF CELLULOSE AND COMPONENTS

#### ISOLATED FROM WOOD

##### 1. THE NITRATION OF XYLAN

In view of the still-existing confusion in the literature concerning the solubility of xylan dinitrate, it was considered desirable to nitrate a sample of xylan under the same conditions as used in the present study of the nitration of wood. A sample of beechwood xylan\* was nitrated in a manner similar to that just described for

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\* The author gratefully acknowledges the gift of this sample from Dr. C.T. Bishop of the National Research Council (Division of Applied Biology) in Ottawa, Canada. For a description of the product, see Appendix II.

the model compounds. Results of the nitrations are shown in Table XXXII.

TABLE XXXII  
The Nitration of Beechwood Xylan by Gaseous  
Dinitrogen Pentoxide

Experiment	Reaction Time (Hr.)	Yield (a) (%)	Nitrogen Content (%)
1	1-1/4	99.57	10.63 (b)
2	3	103.2	- (c)
3	3	94.74	11.23
4	6	96.16	11.17

(a) Most of the preparations suffered a steady and continuous loss of weight, so that no final yield could be calculated. For the method of calculation of the percentage yield, see Appendix III.

(b) All nitrogen contents were determined by a modified Kjeldahl method.

(c) The specific rotation of the acetone-soluble fraction was -24° (at room temperature).

The nitrogen contents of the xylan nitrates reported in Table XXXII were of the same order as those of the best preparations reported in the literature (209a, 228), but were still significantly lower than the 12.6% required theoretically for xylan dinitrate. It is possible that these low results may be a function of the method of isolation of the xylan. It is well known, in the case of cellulose, that the physical state of the preparation greatly affects

the amount of nitrogen which may be introduced by a given reagent (2b, 56, 83d, 341, 342).

The behaviour of the nitrated xylan was different from that of the other polymeric materials nitrated. Except in the case of the product from Run 2 (Table XXXII), the products suffered continued loss of weight of such magnitude that it was felt that determination of the usual "final weight" was unjustified. In general, the yield of product had fallen to 80-85% after storage for approximately a week in a vacuum desiccator, over phosphorus pentoxide and solid potassium hydroxide. Even the material recovered from acetone solution showed a continuous loss of weight. This seeming instability of xylan nitrate, which has not been reported previously, made it difficult to calculate the exact solubility, but, using the same weight as was used to calculate the specific rotation, the solubility was seventy percent in acetone. Complete solubility of the product was not, of course, expected, because of the inorganic material present (Appendices II and III). It should also be mentioned that the residue from treatment with acetone was not completely soluble in water, as would be expected if only inorganic nitrates had been undissolved. Because of the steady loss of weight of this sample, it was felt that a determination of the nitrogen content of the acetone-soluble material would not be meaningful.

It is suggested that the variation in solubility of xylan nitrate preparations may depend upon their method of preparation. The recent work of Schoettler (355) lends emphasis to this point. Schoettler found that the alkali-resistance of xylan seemed to depend

upon the physical structure of the fibre. If this is so for the alkali solubility of xylan itself, it may also be true with respect to the solubility of the nitrate in organic solvents.

## 2. THE NITRATION OF HOLOCCELLULOSE

Holocellulose was prepared from extractive-free western red cedar heartwood by the method of Wise, Murphy and D'Addieco (407). Difficulty was experienced in obtaining reproducible yields. However, the average of five separate determinations was 67.7% which compared well with the 67.4% (408) and 66.0% (260b) previously reported for western red cedar whole wood. The preparations were pure white, and had retained their particulate structures. On nitration, the samples of holocellulose became slightly yellow, indicating the presence of nitrated protolignin. Yields and nitrogen contents of the nitrated holocelluloses are reported in Table XXXIII. The products, although swelled, still retained their original particulate appearance. Qualitative determinations showed the nitrated holocellulose to be incompletely soluble in acetone.

## 3. THE NITRATION OF LIGNIN

Klason lignin was prepared from extractive-free western red cedar heartwood by Tappi method T13 m-54. Duplicate determinations were in good agreement, to give the value of 33.6%. This again agrees well with the reported 32.5% (408) and 32.6% (260b) for western red cedar whole wood (extractive-free). The lignin thus

TABLE XXXIII

The Nitration of Holocellulose and Lignin from Western Red Cedar  
Heartwood, with Gaseous Dinitrogen Pentoxide

Wood Component	Reaction Time (Hr.)	Weight Ratio (a)		Nitrogen Content (%) (b)
		Initial	Final	
Holo-cellulose	1-1/4	1.779	1.725	12.96
	6	1.781	1.697	12.65
Lignin	1-1/4	1.670	1.475	7.15
	4	1.670	1.443	8.07
	6	1.640	1.489	7.36

(a) Calculated as the ratio of weight of the nitrated product to that of the starting material.

(b) Average values, determined by a modified micro Kjeldahl method.

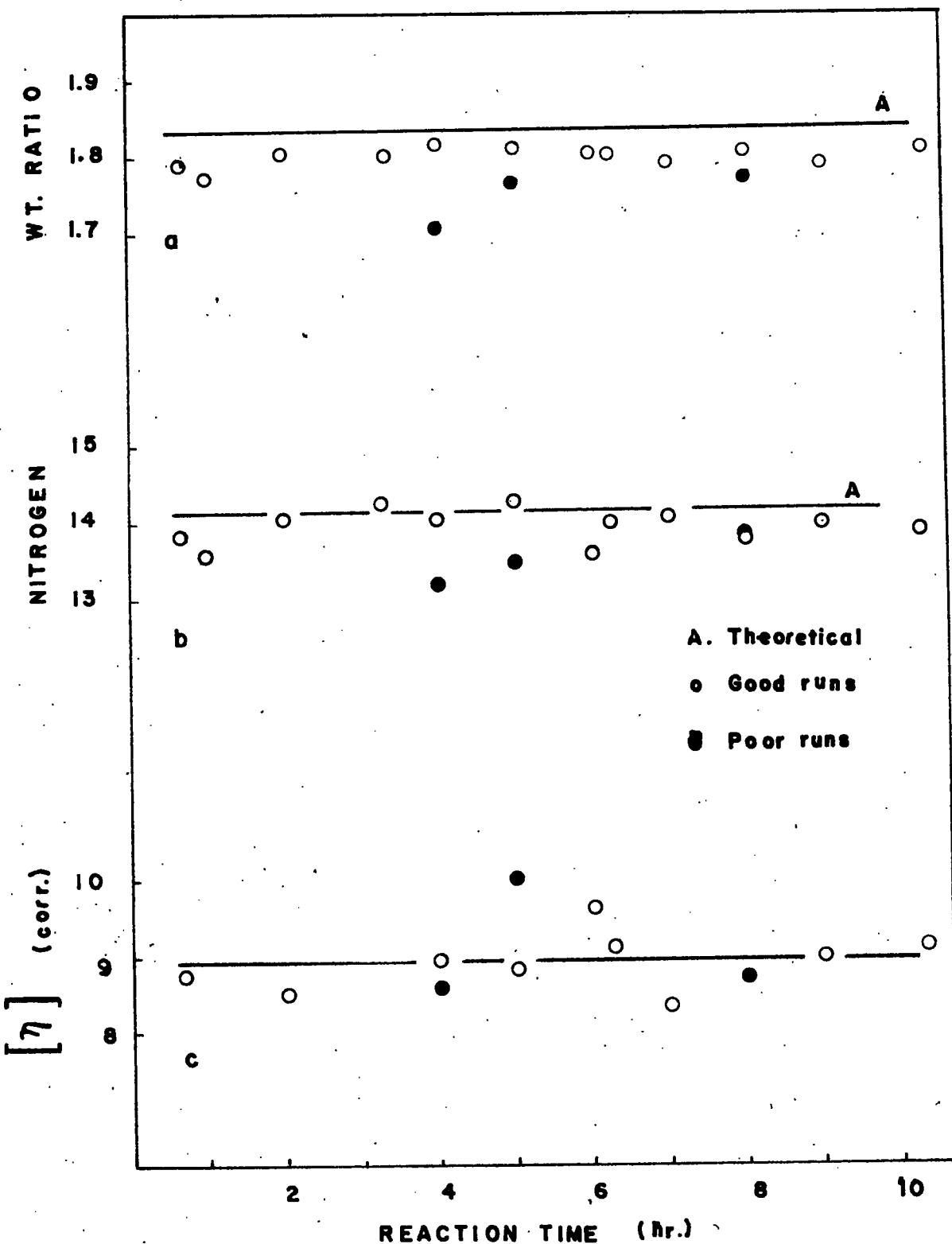
prepared was a very dark brown powder which, on nitration, became a brick red color. The yields and nitrogen contents are shown in Table XXXIII. There was no steady and continued loss of weight of these products, as had been found with salicylic acid, vanillin and vanillic acid. Qualitative determinations showed that the nitrated lignin prepared by treatment of lignin with gaseous dinitrogen pentoxide for seventy-five minutes was incompletely soluble in methanol. The other two samples went into solution in methanol immediately and completely. There is no apparent reason for this difference in solubility, based on either the increase in weight of the lignin on nitration or on the nitrogen content of the samples.

#### 4. THE NITRATION OF CELLULOSE

The Nitration of cellulose by gaseous dinitrogen pentoxide has been reported several times (99, 272a, b, c, 393). Jullander (227) repeated the work of Dalmon, Chedin and Brissaud (99), and found that, although a high content of nitrogen had been introduced, the product had been degraded. Bennett and Timell (32a) likewise found that solutions of dinitrogen pentoxide in carbon tetrachloride, both with and without the addition of phosphorus pentoxide caused degradation of cellulose. On the other hand, Vollmert (393) had shown that pectin was converted to the nitrate in a polymer-analogous manner, on treatment with gaseous dinitrogen pentoxide. It was therefore considered that the preparation and study of cellulose nitrate obtained by means of reaction with gaseous dinitrogen pentoxide would yield much useful information concerning not only its efficiency as a nitrating agent but also its degradative effects. Accordingly, a series of nitrations of cellulose was carried out. The starting material was absorbent cotton which had been dried to constant weight in vacuo over phosphorus pentoxide. The samples were nitrated in the usual way, varying the reaction times from forty minutes to ten hours. Results of this work are shown graphically in Figure III and are tabulated in Appendix IV. The highly-electrostatic products were colorless and had the same physical appearance as before nitration, although the individual fibres seemed to be less flexible. The products were not stabilized in any way (see Appendix V). Attention was focused on three properties; the weight increase, the nitrogen contents of the products, and the viscosities of their acetone solutions.

FIGURE III

The Nitration of Cotton Cellulose with Gaseous Dinitrogen Pentoxide



As was found for all other compounds whose nitration was studied, the weight of the products decreased slightly from the initial value, but generally came to a "constant" final value after two to four days of storage. Samples which had been nitrated under conditions which were not entirely optimum required a longer time in which to attain this constancy of weight. After the initial rapid loss of weight, the rate of loss decreased, but weight loss did not cease. It is these "constant" weights which have been plotted in Figure IIIa. The average weight increase (for the nitrations which took place under optimum conditions) was  $1.800 \pm 0.009$ , the extreme deviations being +0.013 and -0.027. Reactions which, for one reason or another, were considered not to have occurred under optimum conditions, generally exhibited a lesser increase in weight. The ratio of the weight of cellulose trinitrate expected from a given weight of cellulose is 1.833.

These results showed that the nitration of cellulose with di-nitrogen pentoxide was quite reproducible. The fact that the theoretical increase in weight was not obtained was probably of minor importance, since the starting material was absorbent cotton rather than a chemically non-treated cellulose. Of great importance, however, was the lack of any trend toward larger weight increases with increasing time of reaction, which was an indication that hydrolytic cleavage did not take place with the consequent freeing of hydroxyl groups which would then be substituted.

Values for the nitrogen contents of the cellulose nitrate products (Fig. IIIb) (determined by a modified Kjeldahl method (56)) showed a

certain amount of scatter and, in general, were lower than the 14.14% required for cellulose trinitrate. The average nitrogen content of the products prepared under optimum reaction conditions was  $13.94 \pm 0.20\%$ . Extreme limits were +0.35 and -0.40. In considering the significance of these results with respect to the use of dinitrogen pentoxide as a nitrating agent, cognizance of the following factors must be taken. (1) Processing of the cellulose to produce absorbent cotton would probably have altered the chemical structure so that the theoretical amount of nitrogen would not be introduced. (2) The slow but steady loss of weight which continued after the initial, rapid loss, has already been mentioned. The magnitude of this loss can be seen from Appendix IV, wherein are tabulated the weight ratios at the time the sample was taken for analysis. In some cases, the loss was quite significant and, although no attempt was made to determine the cause, the odor of oxides of nitrogen was always detectable in the desiccator in which the products were stored. Since loss of weight (which was almost certainly connected with loss of nitrogen) did not occur to the same extent for all products, it was not surprising that there was a certain amount of scatter in the values for the contents of nitrogen. (3) Great difficulty was experienced, all through the work reported here, in achieving satisfactory analyses for nitrogen. A discussion of this factor is given in Appendix X. It was perhaps unfortunate that the existence of these factors prevented a more rigorous assessment of the nitration of cellulose with gaseous dinitrogen pentoxide. However, it may be said with certainty, in agreement with the literature, that gaseous

dinitrogen pentoxide is capable of nitrating cellulose to a very high degree and that, no doubt, nitration to the theoretical degree was achieved in this work, but was masked by other factors. It is again significant that there was no trend towards either higher or lower contents of nitrogen with increased reaction time, which indicated absence of oxidation and depolymerization. In this respect, attention may be drawn to a tracing of the infra red spectrum of sample C47 (Appendix IV), which is shown in Figure VI. (In obtaining the original tracing of the spectrum, the solid cellulose nitrate was suspended in a nujol mull.) The absence of an absorption band for free hydroxyl groups indicated that substitution was complete and absence of a band for carbonyl groups indicated that no oxidation of chain units had occurred.

Having established that a very high and, in all probability, complete substitution of cellulose was possible under the experimental conditions employed, it was necessary to consider in greater detail the question of chain degradation during reaction. This was accomplished, in the manner which has become standard when dealing with polymeric carbohydrate material, by determination of the viscosity of cellulose nitrate in solution. (For a discussion of the method used, see Appendix VI.) Results of the determinations are shown graphically in Figure IIIc. There was some scatter, the average value being  $9.11 \pm 0.48$ , with extreme limits of +1.6 and -0.88 dl/g. The scatter was probably caused by inaccuracies in the determination of the concentration of the solutions employed. Only small samples of cellulose nitrate were available, so that the amounts to be weighed out were small.

The factor of greatest importance here was the complete lack of any trend towards lowered viscosities: therefore, in agreement with the work of Vollmert (393), it has been shown that cellulose may be nitrated in a polymer-analogous manner by use of gaseous dinitrogen pentoxide. It must be realized, of course, that this statement applies only to samples subjected to the influence of gaseous dinitrogen pentoxide for periods of up to ten hours. However, as this time is more than sufficient to allow complete reaction to occur, the preceding general statement is, in fact, true.

It might be argued that these determinations were not meaningful, since they were carried out on samples of cellulose nitrate which had been stored for some time, during which the presence of oxides of nitrogen could have exerted a "levelling" effect, by causing depolymerization to a given extent in all cases. Unlikely as this appeared to be, it was decided to gather further evidence by checking the viscosity of a solution of freshly-prepared nitrate. As a further check, cellulose nitrate was prepared (from the same sample of cellulose) by the method of Bennett and Timell (32a). Results of viscosity determinations on these samples are shown in Table XXXIV. Within the limits of experimental error, viscosities of solutions of cellulose nitrate products prepared by both methods were the same, and certainly no higher than those of samples which had been stored for some time.

Proof of the polymer-analogous nature of nitration based on viscosity determinations is, of course, not rigorous. However, the proof offered here is of the same status as that extant for other

TABLE XXXIV  
Comparative Studies on the Viscosity of Solutions  
of Cellulose Nitrate

Nitrating Agent	Reaction Time(Hr.)	Nitrogen Content (%)	Weight Ratio		Viscosity (a)	
			Initial	Final	Found	Corrected
Bennett-Timell	3	13.83	-	1.766	6.74	7.46
	3	13.67	-	1.744	6.14	7.16
Dinitrogen pentoxide	1	13.48	1.794	1.679	6.57	8.13
	1-1/4	14.06	1.885	1.813	7.14	7.34

(a) The method of determination is discussed in Appendix VI.

nitrating agents. The occurrence of an initial, rapid depolymerization of, say, particularly "weak" and susceptible bonds is not ruled out. However, as has been pointed out by both Harland (174) and Bennett and Timell (32a), it is unlikely that such a reaction could occur to the same extent, in all instances.

Thus far, a discussion of those nitrations which were considered not to have occurred under optimum conditions has been omitted. (These are shown in Figure III as • .) As was expected, increases in weight and the nitrogen contents were generally lower than for the products of reactions which went well. Unexpectedly, the corrected values for intrinsic viscosity were similar to those for the better runs. These results are remarkable in view of the statement by Bennett and Timell (32a) that lower oxides of nitrogen bring about

depolymerization of cellulose nitrate. The presence of dinitrogen tetroxide during these reactions was indicated by the color of the vapor.

Results for the two forty-minute runs may also be puzzling at first glance. The results of run C-41 are in line with those obtained at other reaction times, while both the weight increase and the nitrogen contents of product C-42 were much lower. These seemingly inconsistent results are readily explained when it is considered that the "reaction times" listed were the total times during which the reaction system was stored in the refrigerator. During this period, it was necessary for the dinitrogen pentoxide to sublime, distil into the reaction flask and then to react with the cellulose. Since nitration occurred very rapidly, a difference of a few seconds in the time in which the dinitrogen pentoxide was in contact with the cellulose would be important. The temperature in the refrigerator varied to a certain extent, so that conversion of solid to gaseous dinitrogen pentoxide occurred, no doubt, at different rates of speed.

## 5. CONCLUSIONS FROM THE PRELIMINARY EXPERIMENTS

The results of the work reported here may be summarized briefly.

(1) With few exceptions, the nitration of simple carbohydrate materials may be brought about more readily and in better yield by use of the more conventional nitrating agents, than by use of gaseous dinitrogen pentoxide. The reason for this result was not apparent, since no detailed investigation of the products was carried out. It

seemed unlikely that the side reaction was hydrolytic, since dinitrogen pentoxide would so readily bind any water formed. The suggestion of oxidative decomposition was still valid. (2) For nitration of compounds in the aromatic series, dinitrogen pentoxide was a useful reagent in some instances only. It seemed not to differ from other nitrating agents in its reaction to cleave a carbon-carbon bond in compounds containing the vanillyl nucleus, where the group para (and also ortho?) to the free hydroxyl is an aldehyde or acid function. (3) With respect to the convenience of handling small quantities, the reproducibility of results, the absence of loss of product to a solution medium, the high degree of substitution obtained and the non-depolymerizing reaction, gaseous dinitrogen pentoxide seemed to be a reagent eminently suitable for the nitration of polymeric carbohydrate material.

#### D. THE NITRATION OF EXTRACTIVE-FREE WESTERN RED

##### CEDAR HEARTWOOD

###### 1. PREPARATION OF THE WOOD MEAL

The method of preparation of the extractive-free wood meal has been described in the section on experimental methods. The wood meal originally prepared, but extracted in several batches, was used for all the work described here.

It has been shown that, under normal drying conditions, the amount of bound water retained by the wood is probably less than one percent (406b) so that, in the presence of gaseous dinitrogen pentoxide, a powerful desiccating reagent, the reaction should have been anhydrous.

## 2. THE NITRATION REACTION

Nitrations were carried out under the conditions established as optimum for the preparation and use of dinitrogen pentoxide by the work on mannitol and cellulose. Because of the low density, samples of the wood weighing up to two hundred milligrams could be nitrated successfully, which was a great improvement over the small amounts of model substances which could be used. The wood was weighed into dried, tared vials, of which as many as six could be accommodated in one reaction flask.

Nitration occurred very rapidly. Immediately upon contact with the dinitrogen pentoxide vapor, the wood became brown and began to swell and, within half an hour of commencement of the reaction, it had increased its volume by approximately one-half. As reaction proceeded, the color of the product gradually lightened until it was a golden brown. The color of the product served as a qualitative indication of the success of a particular nitration, since those conducted under non-optimum conditions yielded products which had retained this brown color to a greater or lesser extent. In all cases, the original particles of wood seemed to be preserved intact.

Removal of excess dinitrogen pentoxide by the method of freeze-distillation which has already been described, was followed by evacuation of the system (for one-half hour) by a pump capable of lowering the pressure to one to two millimeters of mercury. The weight of the product immediately after removal from the reaction flask was used to calculate the ratio hereafter termed the initial weight increase. As already described for several other preparations,

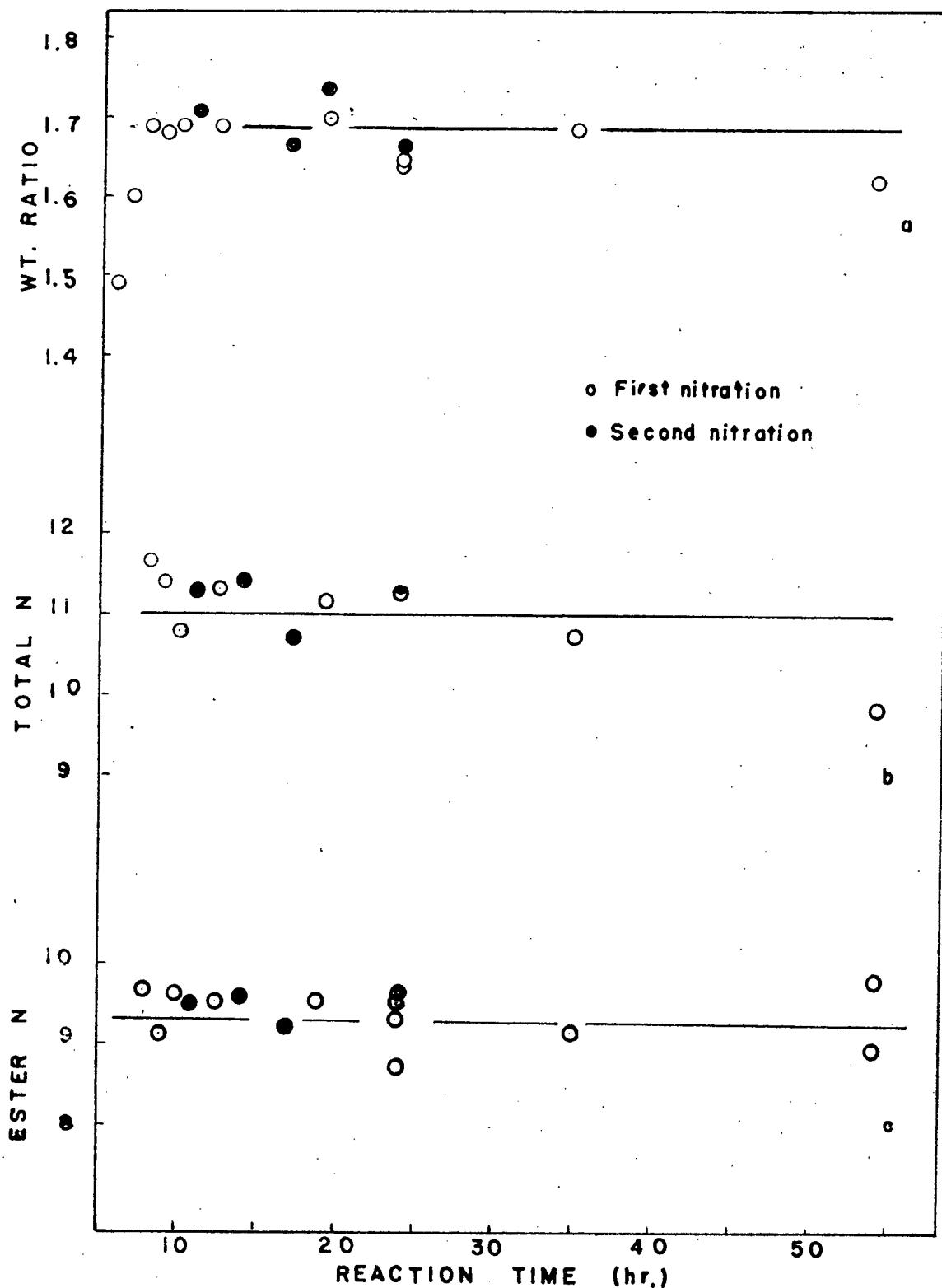
the products were stored in vacuo over phosphorus pentoxide and solid potassium hydroxide. Also, as previously described, a loss in weight continued for two to four days in the case of products of successful runs, but longer for products of unsuccessful runs. The weight ratio of the product, when rapid decrease in weight had ceased, was used to calculate the final ratio. Also parallel to the behaviour of the cellulose nitrates prepared in the present work, there was slow and continuing loss of weight beyond four days, so that yet a third weight ratio was calculated—one which was based on the weight of the preparation at the time a sample was taken for analysis.

The nitration of wood was studied in three series of reactions. The object of the first series (Series A) was to establish optimum reaction times for the nitration of wood with gaseous dinitrogen pentoxide. The results of these reactions are shown graphically in Figure IV, and are tabulated in Appendix VII.

The reproducibility of the reaction, within the range of reaction times from eight to twenty hours is shown in Figure IVa, where the final weight ratio is plotted against the time of reaction. A constant weight ratio of 1.69 was found. Products which, for one reason or another, had not increased in weight sufficiently to give the ratio of 1.69 were subjected to a second treatment with gaseous dinitrogen pentoxide. By this treatment, weights were increased (over those of the original products) but the weight ratios were neither constant nor the same as that found to result from reactions which had been successfully completed during the first reaction period. This could be attributed to at least two causes: (a) nitrations which

FIGURE IV

The Nitration of Extractive-Free Western Red Cedar Heartwood with Gaseous Dinitrogen Pentoxide: Series A



did not proceed under optimum conditions were probably accompanied by side reactions giving products which were chemically altered so that uptake of nitrogen could not occur to the same extent as for the original wood; (b) the necessity for carrying out two reactions allowed a much longer time of contact between wood and dinitrogen pentoxide, during which undesirable side reactions could occur. The low ratios for the six- and seven-hour runs were assumed to be due to reaction periods of insufficient duration to allow completion of reaction. It is possible that the lowered weight ratios noted for products of reactions which lasted for more than twenty hours were caused by denitration. No such effect was noted elsewhere in the present work although these were the only reactions which were allowed to proceed for this length of time. Whether or not de-nitration was brought about by long exposure of the nitrated product to gaseous dinitrogen pentoxide mattered little since nitration of the wood was completed in a much shorter period of time than would be required for this effect to manifest itself. Reactions of up to ten hours' duration gave no sign of denitration when mannitol was the test substance.

The values for total and ester nitrogen contents for samples of Series A are shown in Figure IVb, c. Total nitrogen was determined by a modified micro Dumas method (302) and ester nitrogen by use of a modified Dupont nitrometer (117). The difference between total and ester nitrogen was assumed to represent the content of nitrogen bound to aromatic nuclei as nitro ( $C-NO_2$ ) nitrogen. This assumption was in line with the assignment which was general in the literature

(54b, 248b), although Hibbert and Marion (196) found that nitrated spruce glycol lignin contained nitrogen in the form of both nitro and nitroso (-NO) groups as well as an appreciable amount in an unknown form. There was some scatter in the values for nitrogen content, but this was considered to be less significant than would be assumed from an examination of the plot since great difficulties were experienced in obtaining accurate analyses of nitrogen (Appendix X). It was noticed that, in general, the contents of total and ester nitrogen were parallel, i.e., a high content of total nitrogen generally accompanied a high content of ester nitrogen, and was a further indication that the reaction was reproducible.

It was also noticed that, as expected, the weight ratio varied directly with the content of nitrogen. This suggested that the weight ratio might serve as a more-or-less quantitative indication of the nitrogen content of the product. Since it was recognized that proof of this would be most useful, both because of the experimental errors found in carrying out determinations of total and ester nitrogen and because the Dumas method for determining nitrogen was so time-consuming, further investigation was warranted. To this end, a second series of reactions (Series B) was carried out, each sample being nitrated under conditions which were as nearly identical as it was possible to make them. It was also intended that the results of Series B reactions should show whether or not the reaction could be made entirely reproducible. The information gained from analyses of the products of Series A reactions indicated that maximum weight increase and maximum uptake of nitrogen occurred when the reaction

was allowed to proceed for eight hours. Accordingly, an eight-hour reaction time was chosen. It was during the course of this series of reactions that attempts to use more than one small tube with wood in each reaction flask were first made and found to be successful. In all, nineteen nitration reactions were carried out, to give a total of twenty-seven separate products.

Results of Series B nitrations are tabulated in Appendix VIII. It was considered that thirteen of the samples of nitrated wood had been prepared under conditions which were optimum. The average weight ratio for these was  $1.66 \pm 0.01$ , with extreme values of  $+0.03$  and  $-0.04$ . The average content of ester nitrogen was  $9.15 \pm 0.33$ , with extreme values of  $+0.47$  and  $-1.19$ . A further thirteen samples were nitrated under conditions which seemed to be optimum, although the weight increases were less than expected. It was considered that the poor results had been caused by the use of samples of wood which were too large to allow adequate penetration of the nitrating gas. Accordingly, the products were divided into smaller samples and renitrated. It was found that, although the weight was increased (in agreement with the behaviour of Series A samples on renitration), the weight ratio was neither so constant nor so high as that for products of one nitration under optimum conditions. The average weight ratio for the renitrated products was  $1.63 \pm 0.03$ , the extreme limits being  $+0.05$  and  $-0.14$ . The corresponding values for the content of ester nitrogen were  $9.19 \pm 0.16$ ,  $+0.31$  and  $-0.35$ .

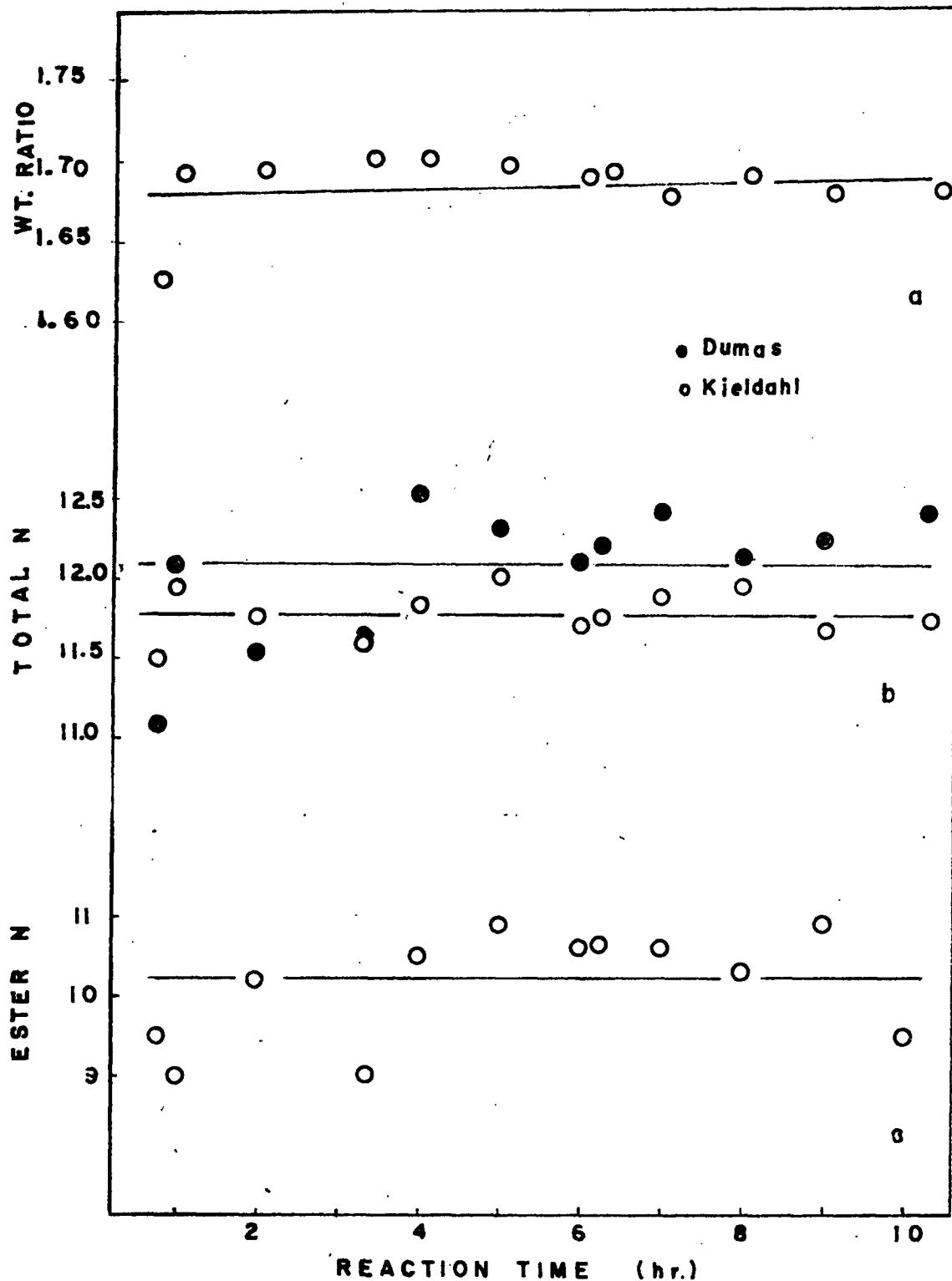
These results showed that, under standardized reaction conditions,

the nitration of wood with gaseous dinitrogen pentoxide could be made reproducible within rather narrow limits, especially with respect to the weight increase. Because of the relatively unreliable method for determination of the contents of nitrogen, the reproducibility of the amount of nitrogen introduced was not as clear. However, even in that respect the range of values obtained was quite narrow.

It was decided to study the nitration of whole wood yet more closely by carrying out a third series of reactions, varying the reaction time within the range which, from Series A, seemed to give products of maximum nitrogen content. Series C nitrations were carried out with four objectives in mind: (1) to verify that the optimum time for reaction had been found; (2) to study even more closely the reproducibility of nitration; (3) to attempt to establish the order of bonding (i.e., which of O- or C- nitrations occurred more quickly); (4) to make a more rigorous comparison between the nitration reaction of wood and of some known compound. Accordingly, samples of cellulose and wood were weighed into separate, tared vials and nitrated, in pairs, in the same reaction flask. These samples were all weighed on a balance capable of weighing to five places of decimals, so that all weight ratios were known to at least four significant figures. All samples of wood were approximately one hundred milligrams in weight, and reaction times were varied within the range of time from forty minutes to ten hours. Results of the Series C nitrations of wood are shown in Figure V and in Appendix IX. (Series C nitrations of cellulose have already been discussed.)

Figure V

The Nitration of Extractive-Free Western Red Cedar Heartwood with Gaseous Dinitrogen Pentoxide: Series 0



In view of the results of the Series A nitrations, it was surprising to find, in Series C, that a nitration time of one hour was sufficient to allow complete nitration of the wood. Since the six- and seven-hour runs of Series A were the first reactions carried out on wood, it was possible that reaction conditions were not at that time optimum, and that the apparent improvement of product with length of time of reaction was due to refinements in technic.

The most important feature of the Series C nitrations was the remarkable reproducibility of reaction which was attained, both with respect to weight increase and to the amounts of nitrogen introduced. The reproducibility was particularly evident in the weight ratios of products of nitrations which took place in the one- to eight-hour range. An analysis of the results is given in Table XXXV. Nitrogen contents also were reproducible, although not as closely as were the weight increases. The amount of nitrogen introduced into the products of Series C reactions was greater than for those of Series A, although the weight ratios were identical. The results show that there was a direct relationship between weight increase and nitrogen content, so that the weight ratio could be taken as a criterion of the degree of substitution of the product.

It was also felt that a sufficient number of samples of wood were nitrated for it to be firmly established that reaction times <sup>found</sup> were optimum for western red cedar heartwood. It was to be expected, from analogy with the behaviour of wood with phosphonitric mixtures (377b), that it would be necessary to establish optimum conditions for each wood species nitrated with gaseous dinitrogen pentoxide.

TABLE XXXV  
Analysis of the Results of Series C Nitrations

Determination	Range of Reaction Times (Hr.)	Average Value	Extreme Limits	
			-	+
Weight Ratio	1 - 6.25	1.693 $\pm$ 0.003	0.008	0.005
	1 - 10.3	1.686 $\pm$ 0.009	0.015	0.012
Total Nitrogen: (%) (Dumas)	1 - 6.25	12.1 $\pm$ 0.3	0.5	0.4
	1 - 10.3	12.1 $\pm$ 0.2	0.5	0.4
Total Nitrogen: (%) (Kjeldahl)	1 - 6.25	11.77 $\pm$ 0.12	0.20	0.25
	1 - 10.3	11.79 $\pm$ 0.12	0.22	0.23
Ester Nitrogen (%)	1 - 6.25	10.1 $\pm$ 0.6	1.1	0.8
	1 - 10.3	10.2 $\pm$ 0.5	1.2	0.7
Non-ester Nitrogen (%)	1 - 6.25	2.0 $\pm$ 0.5	0.6	1.1
	1 - 10.3	2.0 $\pm$ 0.5	0.7	1.1

As found for the cellulose samples, reaction was completed very quickly, the weight increase and nitrogen contents for the products of one-hour reaction being within the range of constancy. In this connection it was noted that, in agreement with the work on cellulose, the forty- to sixty-minute reaction period was critical, showing that reaction was completed soon after the dinitrogen pentoxide vapor

came into contact with the wood. As explained for cellulose also, the lack of agreement between the two forty-minute runs (see Appendix VII) was readily explained on the basis of slight differences in temperature and time of reaction.

The third objective in carrying out the Series C nitrations--to acquire some information concerning the order of reaction of the components--was not realized, due to the paucity of information for short-time reactions, the speed of reaction and inaccuracies in the nitrogen determination. Information gained from analyses of products of reactions which did not go smoothly, and which might have been expected to yield some information concerning the destruction of the wood components, was not conclusive.

It was felt that the results obtained in this study clearly established the efficacy and usefulness of gaseous dinitrogen pentoxide as a reagent for the nitration of whole wood. A survey of the literature showed that no other substitution reaction applied to wood has given results of comparable reproducibility.

Because of the known dependence of substitution reactions not only upon the physical state of the wood but also upon the species, it was difficult to compare results of the present work with those previously reported. Furthermore, the literature contained few reported studies on the chemistry of whole nitrated wood from any source. The earliest study of the nitration of whole wood is that of Friese and Furst (136). By nitrating pinewood with an aceto-nitric mixture, a product of weight ratio 1.65 and containing 10.2% ester and 12.5% total nitrogen was prepared. In the present work,

a sample of extractive-free western red cedar heartwood was nitrated according to the method of Friese and Furst (136). The weight ratio was 1.595, which obviously did not represent the whole wood since both the acetic acid and the methanol washings were colored yellow (in agreement with the reported results for pine wood), and a precipitate was formed on dilution of the wash liquors with water. The nitrogen content (Kjeldahl) was 10.90%. A comparison of this value with the 11.8 - 12.0% nitrogen introduced by use of gaseous dinitrogen pentoxide clearly illustrated the greater efficiency of the gas as a nitrating agent. The non-ester nitrogen content (1 - 2%) of the products prepared by use of dinitrogen pentoxide was slightly lower than that reported by Friese and Furst (2.3%) for nitrated pine wood but was in line with the two percent reported by Brissaud and Ronssin (54b). The western red cedar nitrated by the Friese and Furst method was a dull grey-yellow in color rather than the golden yellow of the wood nitrated with dinitrogen pentoxide.

Nitrated spruce wood was prepared by Lieser and Schaak (263) by use of an anhydrous sulfonitric mixture. The weight ratio of product was 1.59, the nitrogen content 11.8%.

Brissaud and Ronssin (54b) prepared a nitrated spruce wood, with acetonitric mixtures, and obtained a weight ratio of 1.56. The content of total nitrogen was 11.75%.

In comparison with these results, the content of total nitrogen of the nitrated western red cedar heartwood was equal or superior to these values, and the weight ratio was appreciably above any of those

reported. This was probably due, for the most part, to non-loss of material to a solution medium, but might also have been due to increased amounts of nitrogen introduced.

### 3. GENERAL PROPERTIES OF NITRATED WESTERN RED CEDAR HEARTWOOD

The products of all reactions which had proceeded under optimum conditions were a golden yellow color by the time they had become constant in weight. They were very electrostatic, were non-explosive to impact and burned quickly with a bright flame. Although no attempt was made to trace the source of the loss in weight, it was noted that the odor of oxides of nitrogen was always present in the desiccator in which the preparations were stored. Timell (377b) has noted a similar effect when methanol-extracted nitrated wood was stored at room temperature. In the present work, it was found that the decrease in weight was less for preparations which were stored in vacuo than for those stored in a desiccator at atmospheric pressure.

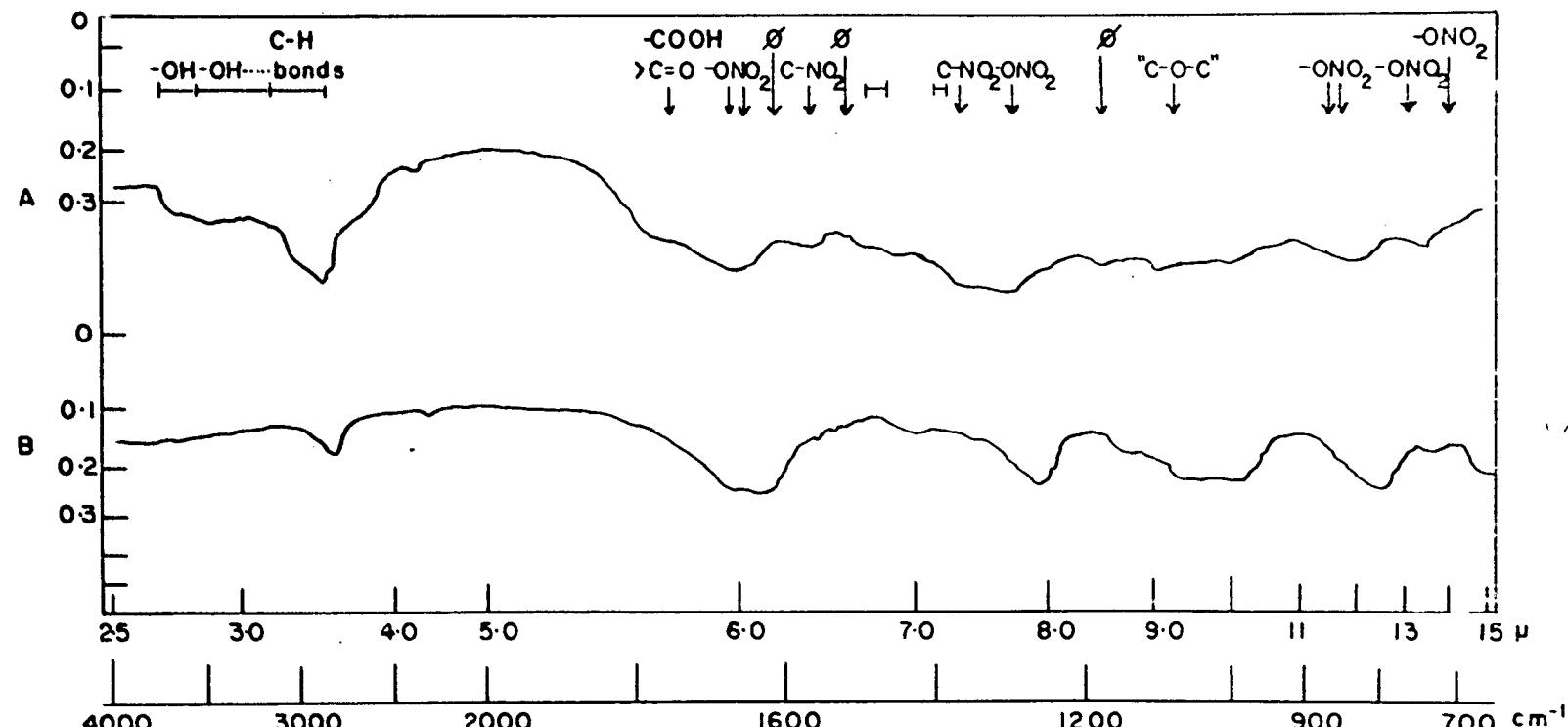
The infra red spectrum of nitrated wood C-47 (suspended in nujol mull) was measured (Figure VI)\*. Although such a complex spectrum does not admit of vigorous interpretation, as yet, it was considered that the absence of peaks corresponding to free hydroxyl and carbonyl groups indicated the completeness of nitration and the absence of oxidation reactions. The presence of both O-nitro and C-nitro groups were indicated. However, attempts to show the presence of

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\* Assignment of the frequencies was made in accordance with information from the following references: 24, 55, 76, 90, 140, 240, 246b, 247, 257, 259, 273, 281, 320, 329, 410, 412. This part of the work was carried out by Dr. L.D. Hayward.

FIGURE VI

Infra Red Spectra of Cotton Cellulose and Extractive-Free Western  
Red Cedar Heartwood Nitrated with Gaseous Dinitrogen Pentoxide



A Nitrated Western Red Cedar Heartwood

B Cellulose Trinitrate

aromatic nitro groups by reduction (of the whole nitrated wood) to amino groups which could be diazotized and then coupled with  $\beta$ -naphthol gave only inconclusive results.

#### 4. QUANTITATIVE ASPECTS OF THE NITRATION OF WESTERN RED CEDAR HEARTWOOD WITH GASEOUS DINITROGEN PENTOXIDE

It was one of the goals of the present work to develop a method for nitration of whole wood which was entirely quantitative. The reaction has been made so with respect to loss of product to a solution medium. This, however, indicated nothing concerning the possible loss of gaseous products such as carbon dioxide, methanol, etc., so that it was necessary to establish some quantitative evidence to show the success achieved. To this end, a series of calculations and determinations of the methoxyl contents of the products was carried out. From the known weight ratios and nitrogen contents, a value for the theoretical weight increase was calculated, assuming that the total increase in weight had occurred because of substitution of hydrogen atoms by nitro groups. (See Appendix XI for a detailed description of the method of calculation.) It was assumed that equality of the calculated and observed weight ratios would indicate uniqueness of reaction, i.e., nitration unaccompanied by side reactions. The results for the three series of nitrations are shown in Table XXXVI. In all cases, the observed weight ratio was higher than the calculated weight ratio by a small and nearly constant amount. This result indicated that the total weight increase was not due to uptake of nitro group nitrogen. Although

TABLE XXXVI  
The Theoretical Weight Ratio for Nitrated Wood

Series	Weight Ratio		Ratio (b)
	Calculated (a)	Observed	
A	1.56	1.63	1.05
	1.61	1.67	1.03
	1.59	1.63	1.03
	1.61	1.65	1.02
	1.60	1.64	1.02
	1.57	1.64	1.04
	1.60	1.65	1.03
	1.60	1.67	1.04
	1.60	1.64	1.03
	1.48	1.57	1.06
	1.57	1.65	1.05
	1.51	1.60	1.06
B	1.61	1.68	1.04
	1.52	1.62	1.07
	1.64	1.67	1.02
	1.61	1.68	1.04
	1.65	1.68	1.02
	1.63	1.67	1.02
	1.62	1.66	1.02
C	1.659	1.693	1.02
	1.632	1.694	1.03
	1.640	1.697	1.03
	1.673	1.698	1.01

(a) Based on content of nitrogen as determined by the Dumas method.

(b) Ratio of observed to calculated weight ratio.

the side reaction most likely to occur would seem to be oxidation, the virtual absence of carbonyl groups (infra red spectrum) indicated that the degree of oxidation was very low. No completely satisfactory explanation for the discrepancy between calculated and observed weight increases has been found.

Although Friese and Furst (136) found that the methoxyl content of pine wood remained constant during its nitration with acetonitric mixtures (3.72% methoxyl in the nitrated product), frequent reference has been made to loss of methoxyl in nitration experiments (137, 417). Methoxyl determinations were carried out on western red cedar heartwood and on its nitrated products to serve as a check on the reaction. The methoxyl content of the extractive-free wood was 6.10%, that of the nitrated wood (of weight ratio 1.638) was 2.23%. Calculated in terms of the weight of the original wood, this latter value would be raised to 3.64%. These values indicated that some demethylation did occur during nitration, at least for this particular sample. The product analyzed was one which apparently had reacted under optimum conditions, although the weight increase was lower than that expected. Although Kurschner (248k) has given evidence that there were no piperonal groups present in protolignin, the author felt that his proof was not conclusive, since the possibility of reaction of the  $O - CH_2 - O$  groups with nitric acid was not considered. Were this to occur, the resulting groups might well resist determination as the usual methoxyl, so that the measured content of methoxyl could, in effect, be lowered without actual loss of methoxyl as gaseous products having occurred. However, this was

purely speculation, since no attempt was made to determine the reality of such an effect. It was shown that the demethylation, if any, did not occur during the time of storage of the nitrated product, since methoxyl determinations made two months apart were in excellent agreement.

Thus, the results of the calculations mentioned above and the determination of the methoxyl content of a single sample of nitrated wood indicate that the nitration of wood with gaseous dinitrogen pentoxide does not occur in a manner which is completely quantitative. This was very disappointing, even though the bulk of the evidence accumulated indicated that the uptake of nitrogen and reproducibility of reaction were superior to any yet reported. No claim was made as to the non-degradative effect of gaseous dinitrogen pentoxide on the carbohydrate constituents of wood. Although this reagent was shown not to cause degradation of isolated cellulose, Bennett and Timell (32a) have shown that only highly purified cellulose may be converted (by means of acetonitric mixtures) to the trinitrate. This would indicate that it is dangerous to extrapolate from the reaction of isolated substances in drawing conclusions as to the effect of a given reagent on wood components in situ.

## 5. PRELIMINARY STUDIES OF THE SOLUBILITY OF WOOD NITRATED BY MEANS OF GASEOUS DINITROGEN PENTOXIDE

The solvents used for extraction of the nitrated wood were anhydrous methanol and anhydrous acetone, which have become "standard" (1b, 62, 377b) for the removal of nitrated protolignin and nitrated

carbohydrate material, respectively. Three sets of extractions have been carried out.

In the first set, parallel determinations were carried out on products (from Series B nitrations, the products of eight-hour runs) which had similar weight ratios and contents of ester nitrogen. The samples were first extracted with methanol (Soxhlet extraction) and the residues from this extraction were treated with acetone at room temperature. Dissolved material was recovered from the solvents by evaporation at reduced pressures and at room temperature. The material extracted by warm methanol was light brown, fairly dense and appeared to be crystalline. However, examination of the extract under a microscope showed that the seemingly crystalline material was, in reality, an amorphous glass. The acetone extracts proved to be dark brown, brittle films (resembling those reported by Dymling, Giertz and Ranby (115)), which, under the microscope were revealed as yellow sheets speckled with dark spots. The residue, although still yellow (indicative of incomplete removal of nitrated protolignin (220)), was lighter in color than the original nitrated wood, and retained its original physical appearance. Yields and analyses of these fractions are shown in Table XXXVII, Columns 1 and 2. The total amount of the nitrated wood dissolved did not exceed twenty-five percent. It should be mentioned that agreement for duplicate determinations of the nitrogen contents of the two extracts were so poor as to be considered indicative of non-uniform samples. This would not be unexpected, since it has been shown that the methanol-soluble material is often a mixture of nitrated protolignin and low-molecular weight carbohydrate material (54b, 188).

TABLE XXXVII

The Solubility of Nitrated Western Red Cedar Heartwood . 1.

Determination	Cold Extraction		Soxhlet Extraction
	1.	2.	
Nitrated wood			
Weight ratio	1.67	1.66	1.67
Nitrogen (%)	9.49 (a)	9.62 (a)	11.7 (c)
Methanol extract			
Weight (%)	18.24	16.52	13.77
Nitrogen (%)	6.98 (b)	6.74 (b)	6.54
Acetone extract			
Weight (%)	6.28	7.42	7.23
Nitrogen (%)	7.85 (b)	9.66 (b)	13.04
Residue			
Weight (%)	75.48	76.06	79.00
Nitrogen (%)	11.53	11.78	11.88

(a) Content of ester nitrogen.

(b) Content of total nitrogen.

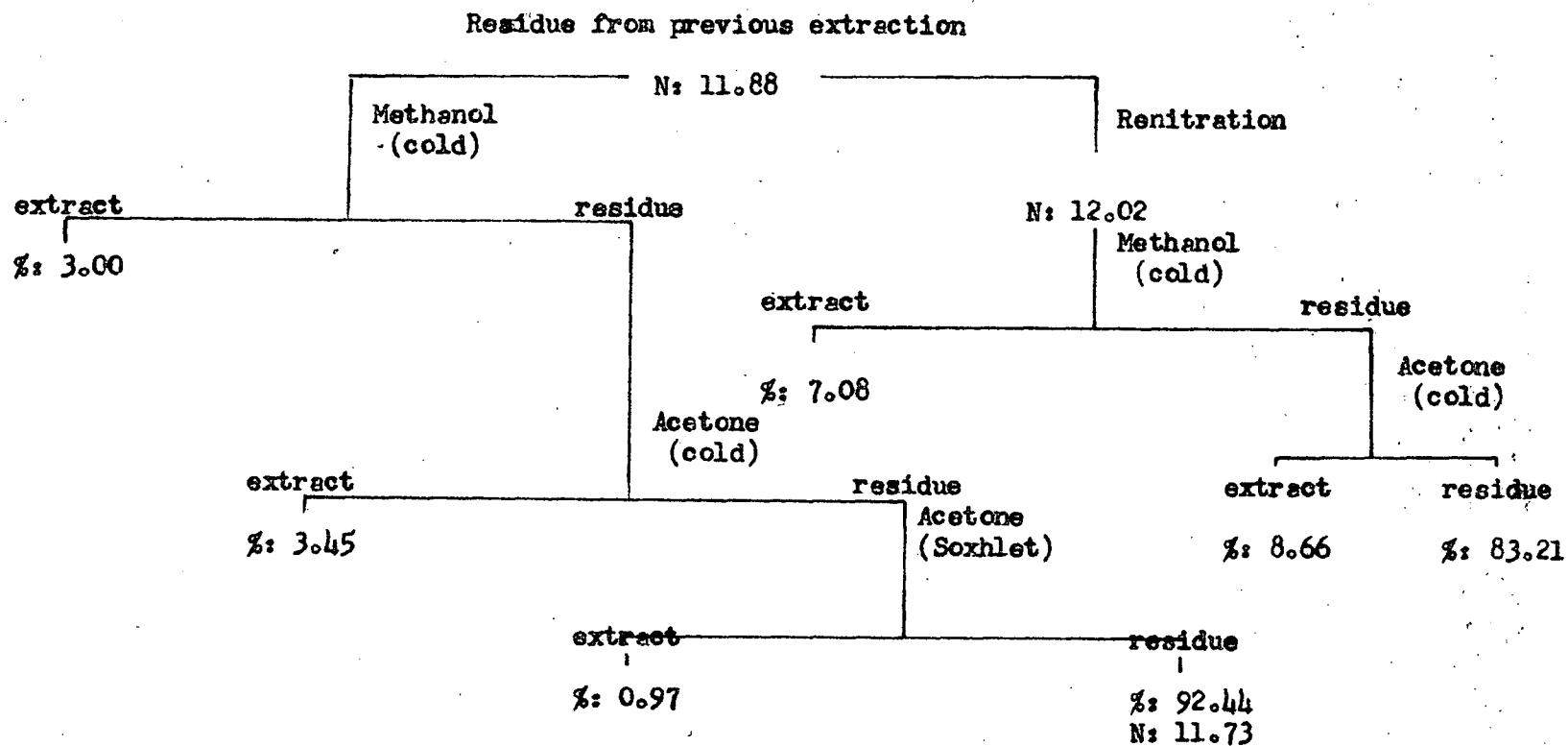
(c) Content of total nitrogen, determined by Dumas method.

In the second series of extractions, a combined sample from Series B products, having an average nitrogen content of 11.7% was studied. This time, both the methanol and the acetone extraction were carried out in a Soxhlet apparatus, so that extractions were made essentially by the warm liquids. Results are tabulated in Table XXXVII, Column 3. Surprisingly, the amount of material extracted by warm methanol was less than that extracted with cold methanol, while the amounts extracted with warm and cold acetone were similar. However, the nitrogen contents of these two acetone extracts varied. In addition, the character of the warm acetone extract differed from that obtained by cold extraction. On evaporation of the solvent, a pliable, opaque, colorless film was found on the sides of the containing vessel, and a brown powder was present in the bottom. The film had a nitrogen content of 13.04%, the powder 11.50%. The material extracted by methanol and the residue were similar in appearance to the corresponding fractions extracted by cold solvents.

Because of the seemingly greater amount of material extracted by cold solvents and the differences in contents of nitrogen, it was thought that it would be interesting to investigate the possibility of achieving a preliminary fractionation by first extracting with cold and then with warm acetone. The ability of the residue from methanol-acetone extraction to take up more nitrogen was also tested, along with the solubility of the renitrated product in the same two solvents. The sequence of extractions is shown in Figure VII. Successive small amounts of the nitrated wood were dissolved out by

FIGURE VII

The Extraction of Nitrated Western Red Cedar Heartwood



recycling through both methanol and acetone, until over thirty percent of the material had been dissolved. There was no evidence available to allow a decision to be made as to the cause of the successive extractions. It could be due to a "layering" effect, so that removal of a layer of nitrated protolignin, for instance, could expose a further layer of nitrated carbohydrate material to the influence of the solvent. On the other hand, although the solvents used were anhydrous, no attempt was made to exclude moist air during changes of solvent so that the continuing solubility could have been the result of slow hydrolysis of high-molecular weight material. Degradation of nitrated carbohydrate material in solution has been reported (see the end of Appendix VI). It will be interesting, in future work, to see how far the method of successive extractions can be carried. Brissaud and Ronssin (54b) carried out a somewhat similar series of alternate extractions, including periodic treatment with hot water, and found that the amounts extracted decreased with each cycle.

The results presented so far show that products formed by treatment of wood with gaseous dinitrogen pentoxide were intermediate in solubility between those prepared by means of phosphonitric mixtures where nearly complete solubility was attained (see Section III-F) and the solubilities of products prepared by use of acetonitric mixtures. Nitrated pine wood was only six percent soluble in acetone (136), nitrated spruce was ten percent soluble in acetone (54b). The nitrated spruce was fifteen percent soluble in methanol, and another nitrated spruce (sulfonitric mixture) was soluble to the

extent of thirty percent in the same solvent (263). Various reasons have been assigned for the incomplete solubility of nitrated wood: the presence of protolignin-carbohydrate complexes (1b, 62), the presence of protolignin, whether or not chemically linked to other constituents (5, 59a, 60b, 377b), and the non-solubility of xylan dinitrate (157, 377b, 378). The present work has thrown no light on this aspect and, indeed, no reason can be assigned for the solubilities found.

The nitrogen contents of the methanol extracts were lower than those found for Klason lignin which had been nitrated by gaseous dinitrogen pentoxide. This result was unexpected in view of the low contents of nitrogen (3 - 3.5%) in nitrated protolignins isolated by Kurschner (248a, b, 251a), and in view of the fact that the methanol extract often contains low-molecular weight material (54b).

Little can be said concerning the nitrogen contents of the acetone extracts. It was quite obvious that they were mixtures, probably containing both cellulosic and hemicellulosic material (3, 115, 120). Considering this, the nitrogen content of thirteen percent observed in one instance for a completely unfractionated sample, compared favourably with the contents of nitrogen observed for fractionated samples of cellulose nitrate isolated from nitrated wood by Timell and his coworkers (365a, b, c, 377b, e). It was not to be expected that cellulose trinitrate would be isolated from wood, since the impurities in cellulose are so many that early workers were confused as to the identity of wood and cotton cellulose (191, 333, 359, 400) by reason of the differences in yield and

nitrogen contents of the nitrates formed by these substances.

In the present work, attempts were also made to correlate the solubility of the nitrated wood with the time of reaction allowed for its preparation. To this end, the samples of wood nitrated in Series C were exhaustively extracted, in turn, by cold methanol and by cold acetone (both anhydrous), and the products were recovered from solution. Also, as previously described, no attempt was made to exclude moist air during solvent changes. Results of this work are tabulated in Table XXXVIII. The values given for the last four samples (No. C-58) show that results were reproducible within one to two percent, which allowed a fairly critical discussion of the other values to be made. It was apparent that samples of low nitrogen content (C-42, 54, 55) were only slightly soluble. One surprising feature of the results was the high solubility for sample C-41, which had been prepared in a forty-minute reaction period. There was a slight trend to lowered solubility as reaction time increased (up to four hours) after which the solubility became almost constant. This result was very interesting in view of the published belief that destruction of protolignin (by oxidation) must precede the solution of its nitration products in methanol (1b, 60b, 292a, 377b). It seemed reasonable to assume that the longer the time of exposure of wood to dinitrogen pentoxide gas, the greater would be the extent of oxidation, demethylation and other degradative changes of protolignin. Granting this, the expected result would be that the more degraded protolignins were more soluble, and that solubility should increase with reaction time. These results must, of course, be

TABLE XXXVIII

The Solubility of Nitrated Western Red Cedar Heartwood . 2.

No.	Reaction Time (Hr.)	Weight of Fraction (a)		
		M (b)	A	R
C41	2/3 (c)	20.96	12.96	65.08
42	2/3	7.32	3.19	88.14
43	1	-	-	-
44	2	17.6	9.36	73.70
45	3-1/3	15.0	8.46	77.91
46	4	16.7	10.79	71.72
47	5	13.8	11.66	76.37
48	6	12.85	7.49	78.66
49	6-1/4	13.4	7.63	77.60
50	7	14.2	7.18	77.84
51	8	13.96	8.32	75.86
52	9	15.4	8.79	74.53
53	10-1/3	13.0	77.29	78.15
54	4 (d)	16.3	3.97	80.65
55	5	8.80	1.26	89.30
56	5	17.1	10.55	72.49
57	8	13.7	8.76	74.59
58	4-2/3 (e)	14.30	7.83	75.01
	"	15.58	8.79	73.12
	"	14.96	8.42	73.92
	"	14.50	8.44	74.32

(a) Expressed as percentage of the nitrated wood originally used.

(b) M: methanol-soluble material; A: acetone-soluble material;  
R: residue. Values are given to the number of significant figures  
warranted by the experimental conditions.

(c) The reaction occurred under optimum conditions.

(d) Reaction occurred under conditions which were not optimum.

(e) Samples nitrated in separate vials in the same reaction flask.

accepted only as being indicative of a trend, since the evidence is yet meagre. However, they would seem to justify further investigation of the variation in solubility of product with reaction time.

In summary, it may be seen that the order of solubility was generally from twenty to twenty-five percent of the wood, although solubilities of up to thirty-five percent have been observed.

## 6. CONCLUSIONS

The following conclusions may be drawn from the work on the nitration of western red cedar heartwood described here:

- (1) The nitration of wood with gaseous dinitrogen pentoxide was a very rapid reaction, and yielded results which were reproducible to a higher degree than any previously reported for substitution reactions with wood.
- (2) Yields of nitrated wood obtained were higher than any hitherto reported.
- (3) A relatively large and reasonably reproducible amount of nitrogen was introduced into extractive-free wood, in the form of both ester and non-ester nitrogen.
- (4) Although strictly quantitative nitration of wood with gaseous dinitrogen pentoxide has not yet been achieved, the method described here approached the ideal more closely than any previously reported.
- (5) The wood nitrated with gaseous dinitrogen pentoxide was soluble to the extent of fourteen to twenty-one percent in methanol, while a further seven to thirteen percent was soluble in acetone. The maximum solubility obtained was just under thirty-five percent.

(6) Fractionation of the whole nitrated wood by successive extraction with organic solvents was found to be feasible and, when combined with the nitration method, comprised a new tool for the study of wood chemistry.

## **APPENDICES**

## APPENDIX I

### SAFETY PRECAUTIONS OBSERVED DURING THE COURSE OF RESEARCH

The method developed by Vollmert for handling dinitrogen pentoxide overcomes difficulties in handling this poisonous material. Other than occasional headaches, no ill effects were noted in working with dinitrogen pentoxide.

Organic nitrate esters are poisonous (when taken internally or absorbed through the skin) and most of them are highly explosive. However, the method of handling introduced here, and the small amounts which were handled at one time, almost entirely obviated the danger from either of these two factors.

The nitration reaction itself, because of the necessity of handling equipment under vacuum, involved a certain amount of danger. In one instance, the distillation loop and its two attached reaction flasks was completely destroyed while in the refrigerator. However, the state of the wood being nitrated, the stage of reaction at which the incident occurred, and the lack of real violence indicated that, rather than an explosion, an implosion had taken place. In order to prevent any further incidents, a set of special, heavy-walled flasks was prepared, and used in all work thereafter and no other accident of this nature occurred.

## APPENDIX II

### THE STARTING MATERIALS FOR NITRATION

The following substances were specially purified before use:  
mannitol, cellobiose,\*  $\beta$ -methyl-D-glucopyranoside, salicylic acid,

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\* Prepared from cellobiose octaacetate, by Mr. E.P. Swan, in this laboratory.

benzoic acid, vanillic acid.

Other compounds of the following grades were used: AR reagents; sucrose, vanillin, tartaric acid; CP reagents; sorbitol, dulcitol, lactose, maltose; Reagent grade chemicals; mandelic acid, fructose.

The sample of xylan, kindly provided by Dr. C.T. Bishop of the National Research Council, was described as follows:

"This material comes from beechwood in the following manner. Holocellulose was made from extractive-free wood by the usual acid chlorite method. This material was then extracted with hot water and this was followed by a 5% aqueous potassium hydroxide extraction. The latter extraction removed the material which I am sending you. It contains 3.84% ash and on hydrolysis yields practically 100% xylose and traces of uronic acid."

### APPENDIX III

#### CALCULATION OF THE THEORETICAL YIELD OF XYLAN DINITRATE

Since potassium hydroxide was used as the extractant, it was assumed that the ash would be potassium oxide. It was also assumed that during the nitration reaction, potassium oxide would react with dinitrogen pentoxide, according to the equation:



The weight increase due to this reaction will be

$$\frac{3.84}{94.19} = \frac{\text{wt.}}{2(101.10)}$$

$$\therefore \text{wt.} = \frac{3.84 \times 202.2}{94.19} = \text{w. per hundred grams of}$$

xylan preparation. From this, the weight of xylan used may be calculated :  $(100 - \text{w.})$ .

$$\text{weight of xylan dinitrate} = (100 - \text{w.}) \left( \frac{222.12}{132.11} \right)$$

$$\therefore \text{weight of product expected} = \text{w} + \frac{(100 - \text{w}) (222.12)}{132.11}$$

APPENDIX IV  
The Nitration of Cellulose  
(Series C)

No.	Reaction Time (Hr)	Weight Ratio <sup>a</sup>			Total Nitrogen (%) <sup>b</sup>	$\eta_{int.}$	
		Initial	Constant <sup>c</sup>	At Analysis		Exp.	Corr. <sup>d</sup>
C 41	2/3	1.850	1.789	1.773	13.80	7.85	8.78
42	2/3	1.576	1.379	1.365	9.84	-	-
43	1	1.836	1.773	-	13.58	-	-
44	2	1.868	1.804	-	14.09	8.33	8.49
45	3 1/3	1.846	1.802	-	14.27	-	-
46	4	1.861	1.813	1.796	14.03	8.60	8.93
47	5	1.853	1.810	1.798	14.29	9.24	8.82
48	6	1.841	1.805	1.800	13.54	7.93	9.63
49	6 1/2	1.819	1.801	1.787	13.99	8.66	9.11
50	7	1.835	1.790	1.803	14.07	8.13	8.33
51	8	1.845	1.807	1.800	13.76	9.51	10.8
52	9	1.823	1.789	1.791	13.93	8.38	8.99
53	10 1/3	1.809	1.860	1.807	13.83	8.26	9.15
54	4	1.907	1.708	-	13.19	6.26	8.58
55	5	1.456	1.280	1.192	-	-	-
56	5	1.823	1.769	1.752	13.50	8.17	10.02
57	8	1.846	1.776	1.789	13.89	8.24	8.78

(a) Calculated as ratio of weight of product to the weight of sample used initially. The theoretical value is 1.833.

(b) Determined by a modified Kjeldahl method. See discussion of this determination further.

(c) The ratio of weights at such time as the rapid loss of weight had ceased.

(d) Corrected to the theoretical nitrogen content.

## APPENDIX V

### STABILIZATION OF CELLULOSE NITRATE

In general, it has been found that commercial preparations of cellulose nitrate (from sulfonitric mixtures) have required stabilization to prevent explosions. In these cases, instability was considered to be caused by the presence of mechanically-held sulfuric acid (83a) which was thought to diffuse into the fibres (71, 79e, f, 83b), and stabilization treatment was designed to wash out this acid. It is now known that the instability resulted from the presence of nitrated oxidation products in the cellulose nitrate (288), so that the term stabilization, in a non-technical sense, has come to mean the extraction of these materials with organic solvents (32a, 258, 294).

## APPENDIX VI

### THE DETERMINATION OF INTRINSIC VISCOSITY

The purpose of the viscosity determinations carried out in the course of the present work was to show whether or not gaseous di-nitrogen pentoxide was capable of nitrating cellulose in a polymer-analogous manner. Therefore, it was felt that only relative values for viscosity were important, and that elaborate equipment was not necessary. All determinations were carried out in a commercially-available Cannon-Fenske viscometer (72) such as recommended by Lindsley (265). The same volume of solution (ethyl acetate) was used for all determination, in which solutions of low concentration (approximately 0.1%) were employed. Intrinsic viscosities were

calculated from single viscosity readings, by the use of the Baker equation (18, 265, 292b), and were then corrected for the deviation of nitrogen content from the theoretical 14.14% (266).

It was not considered that the possibility of decomposition of the cellulose nitrates in solution (21, 211) was important for the present work, since solution of the samples was almost instantaneous. Viscosity determinations were carried out soon after the cellulose nitrate samples had dissolved.

APPENDIX VII

The Nitration of Extractive-Free Western Red Cedar  
Heartwood with Gaseous Dinitrogen Pentoxide: Series A.

No.	First Nitration			Second Nitration			Nitrogen Content (%)		
	Reaction Time (Hr.)	Weight Ratio <sup>a</sup>		Total Reaction Time (Hr.)	Weight Ratio		Total	Ester	Non-Ester <sup>d</sup>
		Initial <sup>b</sup>	Final <sup>c</sup>		Initial	Final			
A 1	8	1.77	1.69	-	-	-	11.56	9.67	1.89
2	9	1.79	1.68	-	-	-	11.40	9.17	2.23
3	10	1.76	1.69	-	-	-	10.78	9.66	1.12
4	12 1/2	1.77	1.69	-	-	-	11.33	9.56	1.77
5	19 1/3	1.79	1.70	-	-	-	11.19	9.58	1.61
6	24	1.75	1.65	-	-	-	11.30	9.38	1.92
7	24	1.79	1.64	-	-	-	9.53	8.76	0.77
8	35	1.84	1.69	-	-	-	10.73	9.16	1.57
9	54	1.80	1.63	-	-	-	9.84	9.01	0.83
10	6	1.60	1.49	11	1.82	1.71	11.32	9.50	1.82
11	9	1.79	1.57	14	1.83	1.74	11.47	9.61	1.36
12	e	1.14	1.04	17	1.81	1.67	10.75	9.25	1.50
13	7	1.685	1.60	24	-	1.67	11.31	9.55	1.76

- a. Weight of product: weight of wood used.
- b. Weight ratio at the end of the reaction.
- c. Weight ratio after the product had come to "constant" weight.
- d. Calculated by difference: total - nitrate nitrogen.
- e. The reaction failed because the vacuum was not maintained during the reaction.

APPENDIX VIII

The Nitration of Extractive-Free Western Red Cedar  
Heartwood with Gaseous Dinitrogen Pentoxide: Series B.

Reaction Time: 8 hrs.

No. (c)	First Nitration Weight Ratio		Second Nitration Weight Ratio		Nitrogen Content (%)			Total: Ester N
	Initial	Final	Initial	Final	Total	Ester	Non-Ester	
B 14	1.80	1.67	-	-	11.34	9.072	2.27	1.25
15	1.80	1.68	-	-	12.10	9.149	2.95	1.32
b 16	1.79	1.67	-	-	-	9.149	-	-
17	1.91	1.68	-	-	-	9.542	-	-
18	1.90	1.67	-	-	-	9.493	-	-
19	1.90	1.67	-	-	11.52	9.148	2.37	1.26
20	1.79	1.69	-	-	-	9.955	-	-
21	1.87	1.65	-	-	-	8.413	-	-
22	1.90	1.66	-	-	-	9.616	-	-
23	1.89	1.66	-	-	11.70	9.593	2.11	1.22
24	1.87	1.65	-	-	-	9.593	-	-
25	1.86	1.64	-	-	-	9.232	-	-
26	1.83	1.62	-	-	-	9.065	-	-
27	1.88	1.63	-	-	-	8.431	-	-
28	1.56	1.20	1.88	1.62	11.47	9.100	2.37	1.26
29	1.61	1.40	1.76	1.66	-	9.242	-	-
30	1.76	1.49	1.76	1.68	9.89	9.437	0.45	1.05
31	1.69	-	1.84	1.66	-	9.067	-	-
32	1.61	1.36	1.82	1.62	12.10	8.838	3.26	1.37
33	1.78	1.66	1.82	1.62	-	9.449	-	-
34	1.61	1.36	1.85	1.59	-	-	-	-
35	1.42	1.22	1.83	1.49	-	8.952	-	-
36	1.70	1.57	1.86	1.66	-	9.230	-	-
37	1.72	1.53	1.86	1.67	-	9.180	-	-
38	1.37	1.23	1.82	1.65	-	9.500	-	-
39	1.37	1.21	1.80	1.64	-	9.016	-	-
40 <sup>a</sup>	1.29	1.16	1.83	1.65	-	8.777	-	-

(a) The vacuum was not maintained. Values are omitted from the averages given.

(b) Samples nitrated in the same reaction flask.

(c) Runs 1-13: conducted under optimum reaction conditions.

Runs 14-26: conducted under optimum reaction conditions, but the samples were so large, that the nitrating gas did not penetrate uniformly.

APPENDIX IX

The Nitration of Extractive-Free Western Red Cedar  
Heartwood Meal with Gaseous Dinitrogen Pentoxide: Series C.

No.	Reaction Time (Hr.)	Weight Ratios			Time Before Analysis (Days)	Weight Loss at Analysis (%)	Nitrogen Contents (%)			Total: Ester N <sup>a</sup>		
		Initial	Final	At Analysis			Total					
							Dumas	Kjeldahl	Ester	Non-Ester		
C 41	2/3 b	1.756	1.625	1.602	-	-	11.1	11.51	9.52	1.6	1.17	
42	2/3	1.462	1.335	1.309	112	1.07	8.34	8.674	5.6	-	-	
43	1	1.789	1.693	-	-	-	12.1	11.94	9.03	3.1	1.34	
44	2	1.807	1.694	1.658	81	2.14	11.6	11.77	10.2	1.4	1.14	
45	3 1/3	1.775	1.697	1.661	81	3.60	11.7	11.57	9.01	2.7	1.29	
46	4	1.755	1.698	1.656	113	2.37	12.5	11.63	10.5	2.0	1.11	
47	5	1.782	1.693	1.657	113	2.10	12.3	12.02	10.9	1.4	1.10	
48	6	1.755	1.685	1.659	106	1.48	12.1	11.71	10.6	1.5	1.14	
49	6 1/2	1.786	1.690	1.656	113	1.99	12.4	11.75	10.7	1.7	1.10	
50	7	1.750	1.673	1.651	116	1.30	12.4	11.88	10.6	1.8	1.17	
51	8	1.767	1.684	1.660	107	1.39	12.1	11.95	10.3	1.8	1.17	
52	9	1.744	1.671	1.644	113	1.48	12.2	11.69	10.9	1.3	1.12	
53	10 1/3	1.687	1.671	1.658	113	1.48	11.9	11.73	9.5	2.4	1.26	
54	4 c	1.859	1.462	1.424	80	2.75	8.47	8.755	7.35	1.0	1.15	
55	5	1.239	1.127	1.084	92	3.74	3.63	2.703	-	-	-	
56	5	1.778	1.659	1.625	106	1.99	11.4	11.47	10.7	0.7	1.06	
57	8	1.769	1.676	1.648	115	1.64	12.3	11.78	10.4	2.0	1.17	
58	4 2/3 d	1.833	1.665	1.645	119	1.24	11.7	-	-	-	-	
	"	1.830	1.659	1.638	119	1.25	-	-	-	-	-	
	"	1.828	1.658	1.638	119	1.23	-	-	-	-	-	
	"	1.830	1.658	1.638	119	1.23	11.2	-	-	-	-	

- a. Based on Dumas value for nitrogen, for comparison with other results.
- b. Optimum reaction conditions.
- c. Optimum reaction conditions not maintained.
- d. Samples contained in separate vials in the same reaction flask.

## APPENDIX X

### THE DETERMINATION OF NITROGEN IN NITRATED CARBOHYDRATES AND WOOD

#### A. THE DETERMINATION OF TOTAL NITROGEN

Since it was desired to make certain that all nitrogen was determined, independent of its form of bonding, the decision was made to carry out analyses by the micro Dumas method. Although organic nitrate esters are known to be difficult to analyze (54b, 254, 292b), a recent modification of the method by Noguchi (302) (the addition to the sample of small amounts of glucose to decrease the rate of combustion) was reported to give good results with compounds of this type. The results of analyses of known compounds, completed in the present work, are shown in Table IA so that the order of accuracy may be more carefully judged.

The values for the analysis of m-dinitrobenzene confirmed that the equipment used was capable of allowing accurate analyses. The low and non-reproducible results for mannitol hexanitrate were not entirely unexpected because of the great lability of the nitrate group at position three (182). However, it was surprising that both mannitol pentanitrate, which no longer has this labile nitrate group at position three, and  $\beta$ -methyl-D-glucoside tetranitrate-2,3,4,6, which is generally considered to be a fairly stable compound (53b) should also show low and non-reproducible results. This indicated that small variations in the contents of total nitrogen in nitrated wood, as determined by the Noguchi micro Dumas method (302) were insignificant, since a large proportion of nitrated carbohydrate material would be present.

TABLE IA

The Determination of the Nitrogen Content in Known Compounds  
by a Modified Micro Dumas Method (302)

Compound Analyzed	Nitrogen Content Required (%)	Nitrogen Content Found (%)	
		Values	Mean
Mannitol hexanitrate	18.58	17.88, 18.01, 17.56 17.60, 17.51, 17.81	17.73
Mannitol pentanitrate	17.20		16.67
$\beta$ -Methyl-D-glucoside tetranitrate	14.97	14.21, 13.97, 13.68 14.73, 14.15	14.15
<u>m</u> -Dinitrobenzene	16.67	16.55, 16.61	16.58

TABLE IIA

The Analysis of Nitrated Western Red Cedar Heartwood by the  
Noguchi Micro Dumas Method (302)

Sample	Total Nitrogen (%)	Sample	Total Nitrogen (%)
A 1	11.00, 12.12, 12.79, 10.69, 11.17	12	10.65, 10.83
2	11.25, 11.54	13	11.23, 11.39
3	10.51, 10.73, 10.83	B 14	11.01, 10.45, 12.25, 11.08, 11.91
4.	11.18, 11.77, 11.03	15	12.06, 12.11, 13.68, 10.52, 12.30
5	10.92, 11.50	19	11.39, 12.05, 11.08
6	11.53, 11.06	23	11.71, 11.45, 11.93
7	9.49, 9.57	28	11.87, 11.48, 11.05
8	10.51, 10.96	30	9.89, 9.88
9	9.92, 9.76	32	11.41, 12.71, 12.18
10	11.41, 11.22		
11	11.45, 11.49		

The non-reproducibility of results in the analyses of nitrated wood is well illustrated in Table IIA, in which are included the actual analytical values for replicate samples. It is the mean of these values which are shown graphically in Figure IV and in Appendices VII, VIII and IX.

In an attempt to gain more accuracy in analysis, a modified Kjeldahl procedure (56) was tested, using first potassium nitrate, and then in parallel analyses with the micro Dumas method. All wood samples in Series C were analyzed by both methods. The individual values are shown in Table IIIA. It was at once apparent that, although the Kjeldahl values were a little lower than the Dumas values, the precision was much greater. For this reason, and also because the Kjeldahl method allowed analyses to be completed much more quickly, the Dumas method was abandoned.

#### B. THE DETERMINATION OF ESTER NITROGEN

Ester nitrogen was determined by the method of Elving and McElroy (117). The known compounds used to test the apparatus were potassium nitrate and mannitol pentanitrate (20 - 40 mg). Mannitol hexanitrate was again shown to be a very unsatisfactory reference compound for the purpose of analysis. Results of the determinations of these compounds are shown in Table IVA, and suggested that the values obtained by this method (in the case of nitrated wood) should be interpreted with caution. Further emphasis was added to this last statement by the deviation of the individual values shown in Table VA. Indeed, so poor was the precision that, in most cases, there was hesitation in even averaging the values, which was done only as a convenience for discussing the results.

TABLE IIIA

Comparison of the Micro Kjeldahl and Micro Dumas Methods

No.	Total Nitrogen Content (%)		
	Cellulose		Wood
	Kjeldahl	Kjeldahl	Dumas
C 41	13.86, 13.74	11.53, 11.49	11.10
42	9.09, 10.64, 9.79	8.62, 8.73	7.96, 8.72, 8.45
43	14.00, 13.19, 13.56 (a)	11.94	11.92, 12.27
44	14.00, 14.17	11.76, 11.78	11.65, 11.44
45	15.13, 14.24, 14.54, 13.92	11.62, 11.52	11.92, 11.40
46	14.39, 13.97, 13.74	11.80, 11.45	13.30, 11.53, 12.76
47	14.26, 14.31	12.11, 11.93	12.56, 12.04
48	13.52, 13.55	11.81, 11.60	11.83, 12.37
49	13.96, 14.02	11.80, 11.70	12.27, 12.45
50	14.22, 14.02, 13.97	12.00, 11.76	12.56, 12.28
51	13.82, 13.70	11.95, 11.95	11.95, 12.31
52	13.90, 13.96	11.60, 11.78	11.95, 12.52
53	13.81, 13.85	11.86, 11.60	11.56, 12.26
54	13.24, 13.26, 13.08	8.77, 8.46	8.61, 7.92, 8.90
55	-	2.67, 2.74	3.90, 3.35
56	13.41, 13.60	11.63, 11.31	11.66, 11.03
57	13.52, 14.27	11.57, 11.98	12.07, 12.58

(a) Dumas nitrogen: 12.91, 13.34

TABLE IVA

The Determination of Ester Nitrogen in Model Compounds

Compound	Content of Ester Nitrogen (%)		
	Found		Required
	Values	Average	
Potassium nitrate	14.0, 13.7	13.9	13.86
Mannitol hexanitrate	17.9, 17.7, 18.4, 20.6, 23.1, 22.5, 20.4, 16.6, 17.0 17.3	19.2	18.6
Mannitol pentanitrate	17.5, 17.0, 16.7, 16.8, 16.6, 17.0, 16.6	16.9	17.2
Cellulose	13.59, 13.35	13.47 *	-

\* Dumas analysis gave 13.55, 13.76 : 13.66.

It was remarkable that both methods for nitrogen which depended upon the measurement of a volume of gas should be so non-reproducible. No satisfactory explanation for this effect has been found.

TABLE VA

The Determination of the Content of Ester Nitrogen in Nitrated  
Western Red Cedar Heartwood

No.	Values	No.	Values	No.	Values
A 2	9.13, 9.20	20	9.76, 10.1	C 41	9.53, 9.50
3	9.94, 9.37	24	9.01, 10.0, 9.00	43	8.81, 8.32, 9.97
5	9.26, 9.78	27	8.15, 9.36, 7.79	44	9.66, 10.2, 10.2, 10.5
6	9.53, 9.23	28	9.30, 8.90	45	8.21, 7.90, 10.9
7	8.74, 8.78	29	9.03, 9.45	46	10.6, 10.4
9	9.25, 8.63, 9.14	30	9.23, 9.64	47	11.0, 10.7
13	9.85, 9.24	31	8.88, 9.26	48	10.6, 10.7
B 14	9.22, 8.92	32	9.14, 8.53	49	10.4, 10.9
15	8.51, 9.79	33	9.11, 9.78	50	10.6, 10.7
16	7.92, 9.59	36	9.31, 9.15	51	10.6, 9.97
17	9.76, 9.33	38	10.0, 9.0	52	10.7, 11.1
18	8.92, 9.99	39	9.31, 8.72	53	9.85, 9.07
19	8.86, 9.35	40	8.56, 9.00	56	11.2, 10.1
				57	10.6, 9.91

## APPENDIX XI

### CALCULATION OF THE THEORETICAL INCREASE IN WEIGHT ON NITRATION OF WOOD

The results reported in Table XXXVI were calculated in the following manner:

Given that the nitrogen content of a preparation is  $N\%$ , and the observed weight ratio is  $W$ , the increase in weight due to uptake of nitrogen will be

$$N \times W \text{ g/g of wood} \quad (a)$$

If it is assumed that all nitrogen was added in the form of  $\text{-NO}_2$  groups, the weight increase due to uptake of oxygen will be

$$N \times W \times \frac{32.00}{14.01} \text{ g/g of wood} \quad (b)$$

The weight of hydrogen displaced will be

$$N \times W \times \frac{1.008}{14.01} \text{ g/g of wood} \quad (c)$$

Therefore, one gram of wood should be converted to  $1 + a + b - c$  grams of nitrated wood, if no oxidation has occurred.

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