was distilled in an 8-in. helix-packed column. The product had the following physical properties: b. p. 40–41° (5 mm.), $n^{20}D$ 1.4153, d^{20} 0.8786, $MD_{obs.}$ 45.21 ($MD_{calcd.}$ 45.43).

This ester yielded an anilide which crystallized from aqueous methanol as long white needles, m. p. and mixed m. p. with diisopropylacetanilide[12] 147–148°.

Anal. Calcd. for $C_{14}H_{19}ON$: N, 6.44. Found: N, 6.64.

Preparation of Isomeric 3-Methyl-2-pentenoic Acids by Method of Kon and Linstead.—Both geometrical isomers of 3-methyl-2-pentenoic acid have been reported[13] and in order to obtain authentic samples of these acids, the preparation from 3-methyl-3-hydroxypentanoic acid was repeated. The unsaturated acids obtained by dehydration with anhydrous hydrogen chloride were partially esterified to remove the β,γ-isomers,[14] and the mixed α,β-acids were obtained.

After redistilling the 3-methyl-2-pentenoic acids, the *cis* and *trans* isomers were separated by fractional crystallization. Four crops of solid were removed from the mixture at successively lower temperatures, and this material proved to be the *trans* isomer, m. p. 46–48°. After long standing, the mother liquor deposited a solid acid, m. p. 13–14°, $n^{20}D$ 1.4651, d^{20} 0.9851. These values are all in excellent agreement with those reported by the previous workers for these acids.[13]

(12) The diisopropylacetanilide used for comparison was prepared by Mr. A. Sacks (dec.) from diisopropyl cyanoacetate.

(13) Kon, Linstead and Wright, *J. Chem. Soc.*, 602 (1934), report for the *trans* acid, m. p. 48–49°; for the *cis* acid, m. p. 12°, $n^{20}D$ 1.4650, d^{20} 0.9830.

(14) The *cis*- and *trans*-3-methyl-3-pentenoic esters were obtained from this fraction in the prescribed manner (for details see ref. (5)).

Both of these acids were converted to the *p-toluides*. The *trans* acid yielded a very clean derivative, which was readily crystallized to a constant m. p. of 78°. The *cis* acid was converted to a *p*-toluide by two methods. In the first method the acid chloride was prepared using thionyl chloride, and the resulting material was treated with *p*-toluidine. In the second procedure, the acid was converted to the methyl ester by means of diazomethane, and the ester was treated with *p*-toluido-magnesium bromide. From both of these reactions a product was obtained which after repeated crystallizations from different solvents had m. p. 61–63°. It is to be noted that this value corresponds with the melting point of the mixed *p*-toluides obtained from the rearrangement products of dibromomethyl *s*-butyl ketone. Thus the *cis* acid and its *p*-toluide melt considerably lower than the corresponding products from the rearrangement and are evidently contaminated with the *trans* isomer.

Summary

1. The Favorskii rearrangement has been applied to four α,α'-dibromo-α-alkyl ketones, and has been found to be a general reaction.

2. Under identical rearrangement conditions, α,α'-dibromoketones yield α,β-unsaturated esters, whereas α,β-dibromoketones yield β,γ-unsaturated esters.

3. The geometrical isomers of 3-methyl-2-pentenoic acid have been definitely characterized, and their properties and derivatives are described.

STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 31, 1949

[CONTRIBUTION NO. 188 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

Investigations on Lignin and Lignification. I. Studies on Softwood Lignin[1]

BY WALTER J. SCHUBERT AND F. F. NORD

Much of the difficulty involved in determining the constitution of lignin can be attributed to the fact that, until relatively recent times, no method was known by which lignin could be isolated in an unchanged form. Whatever procedure was employed, a preparation was obtained which was no longer identical with lignin as it exists in nature.[1a]

The solution to the problem of isolating lignin in a chemically unchanged form therefore requires an approach that avoids high temperatures and employs neutral, chemically inert solvents.[2] Brauns' extraction of Native Lignin from black spruce,[3a] western hemlock[3b] and aspen[3c] with 95% ethyl alcohol at room temperature seems to have met these requirements. However, the failure of approximately 97% of the lignin present to be so extracted[3a] suggests that either this native lignin is not identical with the bulk of the lignin of the wood, or that the residual lignin is associated (either chemically or physically) with the cellulose of wood.

Prior to Brauns' isolation of native lignin, however, a preparation very similar in character to his lignin was obtained by extraction with ethyl alcohol of Norwegian spruce wood which had been rotted by the "dry rot," *Merulius lacrymans*.[4] Thus, these two findings suggested the possibility of utilizing cellulolytic enzyme systems as a convenient method for obtaining larger amounts of native lignin from wood.[5]

It is generally assumed that there are two different types of wood decay brought about by fungi, namely, the "brown" and the "white" rots. In the former, preferential attack is made on the carbohydrate components of the wood, and the lignin remains unaffected, with the decaying residue turning brown in color. In the second type,

(1) Presented at the Wood Symposium of the National Research Council and the Office of Naval Research, Washington, D. C., June, 1949, and before the Division of Cellulose Chemistry of the Am. Chem. Soc., Atlantic City, N. J., September, 1949.

(1a) M. Phillips, in Wise's "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 272.

(2) W. J. Wald, P. F. Ritchie and C. B. Purves, THIS JOURNAL, **69**, 1371 (1947).

(3) (a) F. E. Brauns, *ibid.*, **61**, 2120 (1939); (b) F. E. Brauns, *J. Org. Chem.*, **10**, 211 (1945); (c) M. A. Buchanan, F. E. Brauns and R. L. Leaf, Jr., THIS JOURNAL, **71**, 1297 (1949).

(4) E. C. Barton-Wright and J. G. Boswell, *Biochem. J.*, **25**, 494 (1931).

(5) F. F. Nord and J. C. Vitucci, *Adv. in Enzymol.*, **8**, 253 (1948).

lignin seems to be the main substrate of the fungus, and in the residue, there are patches of a white substance considered to be pure cellulose.

Obviously, then, if an attempt is to be made to obtain lignin after the action of molds on wood, organisms of the first group (*i. e.*, the "brown" rots) must be employed, since these possess a selective cellulose-degrading enzyme system, but leave the lignin unattacked.

Consequently, sound samples of certain species of softwoods were infected with representative members of this class of wood-destroying molds and the effects of the decay of the wood by the microörganisms were progressively followed by chemical analyses of the resulting material. Native lignin was then isolated from this decayed wood. A study of the chemical properties of the lignin so obtained, and a comparison with the properties of certain lignin preparations obtained by the customary methods, comprise the subject-matter of this report.

Experimental

The wood species investigated in these experiments were white Scots pine (*Pinus sylvestris*) and white fir (*Abies concolor*), and the "brown rot" organisms employed to effect the decay were *Lentinus lepideus*, *Poria vaillantii* and *Lenzites sepiaria*.

Sterilization and Inoculation of Wood Samples.—The wood samples were cleaned of their bark, etc., and ground to 60 mesh in a mill. Ten gram samples of the sawdust were weighed into each of several 500 ml. Fernbach-type culture flasks, and to each flask was added a 25 ml. portion of a nutrient medium consisting of:

Neopeptone	1.0 g.
KH_2PO_4	1.5 g.
$MgSO_4 \cdot 7H_2O$	0.5 g.
Thiamine hydrochloride	2.0 mg.
Tap water to	1 lit.

The flasks were plugged with cotton, and, in order to avoid thermal destruction of the wood, sterilized with streaming steam at 100° for thirty minutes on three successive days. After cooling, each flask was inoculated with a 5-ml. spore-mycelial suspension of a pure culture of one of the above organisms, which had previously been cultivated on a solid medium containing the above nutrients, plus 20 g. of glucose and 20 g. of agar. The inoculated flasks were incubated in the dark at 27–28°. The progress of the decay was followed by periodic analyses of the wood residues.

Analytical Methods.—The wood residues were analyzed in duplicate for their cellulose and lignin contents, both of which were corrected for moisture. Moisture and lignin were determined by standard methods,[6] while cellulose was determined by the method of Virtanen and Koistinen.[7]

As the decay proceeded, it became necessary to remove the adhering fungal mycelia. This was accomplished by repeatedly suspending the contents of the flasks in large volumes of water and stirring, whereupon the sawdust settled to the bottom, while the mycelial matter could be decanted from the surface of the water.

Isolation of Alcohol Extractable Lignin.—The method of isolation of lignin was essentially the same as Brauns' isolation of native black spruce lignin.[3a] Thus, sound or decayed 60-mesh sawdust was first extracted thoroughly with cold water and ether. Then, the lignin was isolated by extracting the sawdust with 95% ethyl alcohol at room temperature, in a percolator-type extractor, until the alcoholic extract no longer responded to the "phloroglucinol test" for lignin.[1a] The alcohol was distilled off under reduced pressure, whereupon a resinous material was obtained. This was washed well with water and ether. The resulting powder was dissolved in dioxane, and precipitated into ice-water. The precipitate was dried, redissolved in dioxane and precipitated into ether. This latter precipitation was repeated until the methoxyl content remained constant. The lignin so obtained was a light cream colored powder.

The acetate and phenylhydrazone derivatives of this lignin were also prepared.[3a]

Isolation of Chemically Prepared Lignins.—In all cases, the wood was first freed of "extractives" by extracting the sawdust in a Soxhlet apparatus first with a (1:2) alcohol–benzene solution, and then with water.

Sulfuric acid lignin was isolated in a customary way,[8] fuming hydrochloric acid lignin, according to Kalb and Lieser,[9] and alkali lignin, by a combination of the methods of Powell and Whittaker[10] and of Mehta.[11]

Ultraviolet Absorption Spectra.—Solutions for ultraviolet analysis were prepared by dissolving 3 to 5 mg. of sample per 100 ml. of solvent (90 parts of purified dioxane to 10 parts of distilled water), and diluting as required. The absorption curves were determined with the aid of a Beckman quartz spectrophotometer.

Results

Chemical Effects of the Decay.—The results of the periodic analyses of the decaying wood are presented in Table I. From the data recorded it is obvious that the net effect of the action of these brown rot organisms on wood is indeed a

TABLE I

THE EFFECT OF THE ACTION OF BROWN ROT ORGANISMS ON THE CHEMICAL COMPOSITION OF WOOD

Wood species	Organism	Decay period, (months)	Cellulose, %	Lignin, %
White Fir	*Lentinus lepideus*	0	60.3	24.9
		4	51.2	30.6
		5	47.3	33.8
		6	46.5	36.4
		7	45.8	39.3
White Scots Pine	*Lentinus lepideus*	0	61.7	26.8
		4	49.5	31.8
		5	46.1	37.4
		6	46.0	40.0
		7	39.9	44.9
White Scots Pine	*Poria vaillantii*	0	45.5	33.9
		3	45.4	34.9
		5	33.4	42.1
		8	25.6	46.5
		11	17.6	51.1
		15	15.2	52.5
White Scots Pine	*Lenzites sepiaria*	0	45.5	33.9
		3	39.9	37.9
		6	30.1	41.0
		9	19.5	45.6
		13	18.5	50.1

(6) "Methods for the Chemical Analysis of Pulps and Pulpwoods," Forest Products Laboratory, Madison, Wis., 1939.

(7) A. I. Virtanen and O. A. Koistinen, *Svensk Kem. Tid.*, **56**, 391 (1944).

(8) E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24**, 103 (1932).

(9) L. Kalb and T. Lieser, *Ber.*, **61**, 1007 (1928).

(10) W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **127**, 132 (1925).

(11) M. M. Mehta, *Biochem. J.*, **19**, 958 (1925).

depletion in the cellulose composition of the wood, together with a concomitant increase in the relative content of lignin. This "lignin-enriched," decayed wood therefore seemed to offer a potential source for the isolation of further amounts of virgin lignin.

Alcohol Extracted Lignin.—As stated previously, only about 3% of the lignin content of sound wood can be isolated by alcoholic extraction. It was therefore of interest to determine whether increased amounts of lignin could be extracted from the decayed wood.

Accordingly, the white Scots pine and white fir wood samples, previously subjected to decay by the organism, *Lentinus lepideus*, were then thoroughly extracted with ethyl alcohol at room temperature and, simultaneously, sound samples of the same species of wood were subjected to the same thorough room-temperature, alcoholic extraction. The yields of lignin isolated from the sound and decayed pine, and the sound and decayed fir were 3.2, 6.9 and 2.4, 4.9%, respectively.

Thus, after a seven-month period of decay by *Lentinus lepideus* there is approximately a two-fold increase in the yields of alcohol-extractable lignin from the decayed samples over and above that obtained from the sound wood of the same species. It thus became of importance to determine whether this enzymatically liberated lignin was chemically identical with, or different from, the native lignin isolatable from the sound wood.

Therefore, a comparison was made of the lignin isolated by the method of Brauns[3a] from sound white Scots pine with that obtained from this species of wood after decay by the organism, *Lentinus lepideus*. This comparison involved the elementary compositions, methoxyl contents, solubilities, reducing ability, color reactions and ultraviolet absorption spectra of these lignins, as well as of their acetate and phenylhydrazone derivatives. The results of this comparison are presented in Table II, and the ultraviolet absorption spectra of the two lignins are given in Fig. 1.

TABLE II

COMPARISON OF THE LIGNINS ISOLATED FROM DECAYED AND SOUND WOODS

	Lignin from sound white scots pine, %	Lignin from decayed white scots pine, %
C	64.0	63.7
H	6.3	6.3
OCH_3	15.3	14.5
OCH_3 of acetate	10.1	10.4
OCH_3 of phenylhydrazone	13.3	13.0

Comparison showed that the lignins isolated from sound white Scots pine and from samples decayed by *Lentinus lepideus* were both soluble in methanol, ethanol, dioxane, pyridine, glacial acetic acid, and 4% caustic soda. Both lignins reduced Fehling solution, gave a violet-red color with the phloroglucinol reagent, and yellow colors with the aniline, *p*-phenylenediamine and diphenylamine reagents. The resemblance extended to their analytical data (Table II) and their ultraviolet absorption spectra (Fig. 1).

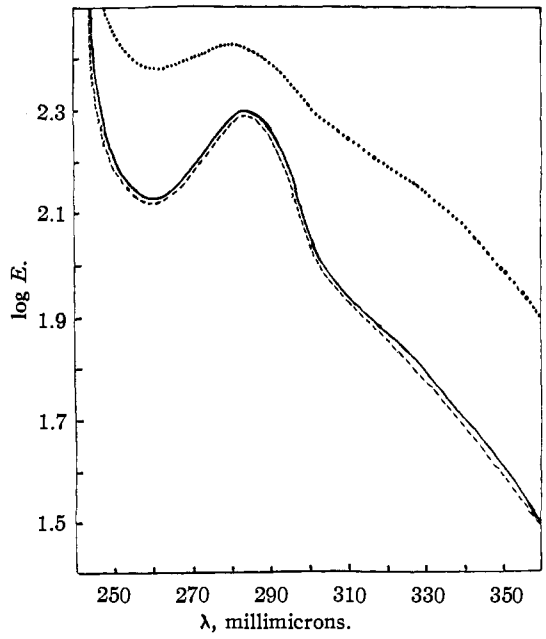


Fig. 1.—Ultraviolet absorption spectra of lignins: ——, lignin from sound white scots pine; ---------, lignin from decayed white scots pine; ....., "Indulin."

From these data, in conjunction with the agreement of the ultraviolet absorption spectra of the two lignins, it may be concluded that the native lignin of white Scots pine wood, and the lignin liberated from this wood by enzymatic degradation of the wood-cellulose are identical.[11a]

A similar comparison was made of the lignins obtained from sound and from *Lentinus lepideus*-decayed white fir wood.

The sound and decayed white fir wood lignins contained 14.8 and 14.5% methoxyl, respectively. Sound and decayed white Scots pine lignins had methoxyl values of 15.3 and 14.5%. Brauns' black spruce lignin had 14.8% methoxyl, while his western hemlock lignin contained 14.7% methoxyl. From the identity of the ultraviolet absorption spectra of the various lignin samples, it appears that the lignin obtained from decayed white fir wood is similar to the native lignin of this species, and moreover that they are also similar to the two lignins from white Scots pine, and also with Brauns' two native lignins.

Chemically Prepared Lignins.—The various procedures described in the literature for the isolation of lignin can be divided into two classes: (1) those that depend on the removal, by hydrolysis, of the cellulose and other constituents of the wood, leaving the lignin as an insoluble

(11a) This seems to obviate "results" by H. and A. Erdtmann referred to in a discussion (*Nature*, **164**, 565 (1949)) at the First Internat. Congress of Biochemistry in Cambridge, England, August, 1949.

residue; (2) those that depend on the removal of the lignin from the cellulose and other substances with which it is associated, by reagents which selectively dissolve the lignin.

Of the methods of the first class, the isolations employing 70% sulfuric acid[8] and fuming hydrochloric acid[9] were applied to white Scots pine wood, while of those of the second group, a procedure employing concentrated alkali at high temperature and pressure[10,11] was used. Moreover, a commercial preparation which has been suggested as a "standard" lignin,[12] namely, "Indulin," was also studied for comparative purposes.

The elementary compositions and methoxyl contents of these preparations and those of our lignins (isolated by alcoholic extraction) are compared with those of Brauns' native black spruce lignin, which has been selected as an independent standard of reference, in Table III. The ultraviolet absorption spectrum of "Indulin" is also presented in Fig. 1.

TABLE III

COMPARISON OF ALCOHOL EXTRACTED WHITE SCOTS PINE LIGNIN WITH LIGNINS OBTAINED BY CHEMICAL TREATMENT

	C, %	(Deviation)	H, %	(Deviation)	OCH_3, %	(Deviation)
Black spruce Brauns[3a]	63.6	...	6.2	...	14.8	...
Alcoholic extraction	64.0	+0.4	6.3	+0.1	15.3	+0.5
Enzymatic liberation	63.7	+0.1	6.3	+0.1	14.5	−0.3
70% H_2SO_4	63.4	−0.2	5.8	−0.4	14.4	−0.4
Fuming HCl	62.1	−1.5	5.3	−0.9	13.2	−1.6
10% NaOH	62.1	−1.5	5.3	−0.9	16.8	+2.0
"Indulin"	64.9	+1.3	5.8	−0.4	15.8	+1.0

From these data, and the obvious difference between the ultraviolet curves of our lignins and "Indulin," it may be realized that none of the chemically obtained lignins resembles native lignin in its chemical composition nearly so closely as does our product obtained by enzymatic decay of wood.

Discussion

We have therefore been able to isolate from enzymatically decayed wood, by a simple extraction procedure involving no elevated temperatures or drastic chemical treatments, a lignin preparation which is identical in chemical composition with lignin as it would seem to exist in nature. This lignin has been isolated in yields superior to those attainable from sound, uninfected wood. It was therefore liberated from its association in the wood as a result of the enzymatic activity of the fungus causing the rot. A detailed study of this preparation could greatly enhance the clarification of the constitution of lignin as it exists naturally.

A comparison of this material with the small amount of native lignin isolatable from wood indicates the identity of the two lignins, in all respects. This finding therefore suggests that native lignin could be considered as representing the total lignin content of the wood.

The objection has been raised[2] that the failure of 97% of the lignin present to be extracted by alcohol from sound wood indicates that native lignin could not be identical with the bulk of the lignin in wood. However, the inability to isolate the remaining part of the lignin by this method is undoubtedly due to some physical phenomenon. Thus, there is much evidence which attests to the presence of a physical union between the lignin and cellulose as they co-exist in wood, in contradistinction to a true chemical linkage. For example, electron micrographs of wood[13] show that lignin has an amorphous-granular structure that exhibits no intimate connection with cellulose, since the fibrils appeared unchanged by extraction.

Moreover, in investigations of bamboo[14] and cottonseed hulls[15] indirect evidence was obtained to support the non-existence of a lignin–cellulose chemical linkage. These results indicated that the carbohydrates and lignin are present as independent and separate chemical entities.

Finally, it should not be overlooked that the assumption[16] that cellulose plays no role in the origin of lignin is unfounded. Thus, the experimentally established formation[17] of methyl *p*-methoxycinnamate by *Lentinus lepideus* from wood, glucose and xylose *via* acetaldehyde[18] corroborates the postulation that the cellulosic fraction of wood serves as the starting point in the carbohydrate–lignin transformation.

Furthermore, the observed disappearance[18] of this crystalline ester from culture-media of *Lentinus lepideus* suggested that a further enzymatic system was providing for the subsequent breakdown of this water-insoluble ester into a simpler product. Thus, it was found that on hydrolysis of an emulsion of methyl *p*-methoxycinnamate (I) with a *Fusarium* lipase,[19] the free acid was obtained.

Further enzymatic degradation of the *p*-methoxycinnamic acid (II) would then result in the formation of some product, such as anisaldehyde (III). The structural similarity of these compounds to such common degradation products of lignin as veratric acid (IV) and vanillin (V), is apparent from their formulas

(12) A. Pollak, in "Lignin Chemistry and Utilization," Bulletin No. 19 of the Northeastern Wood Utilization Council, New Haven, Conn., 1948, p. 65.

(13) K. Mühlethaler, *Biochim. et Biophys. Acta*, **3**, 15 (1949).

(14) M. Lüdtke, *Ber.*, **61**, 465 (1928).

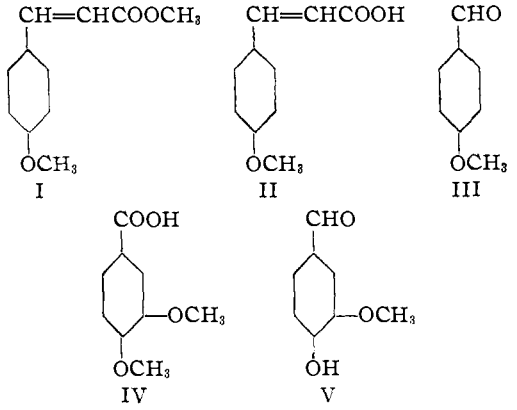
(15) M. A. Smith and C. B. Purves, *Ind. Eng. Chem., Anal. Ed.*, **13**, 157 (1941).

(16) K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 81 (1939).

(17) F. F. Nord and J. C. Vitucci, *Arch. Biochem.*, **14**, 243 (1947).

(18) F. F. Nord and J. C. Vitucci, *ibid.*, **15**, 465 (1947); W. T. Schubert and F. F. Nord, *ibid.*, **20**, 465 (1949).

(19) J. V. Fiore and F. F. Nord, *ibid.*, **23**, 473 (1949).



The enzymatic formation from carbohydrate of a methoxylated aromatic compound thus provides an insight into the mechanism whereby the carbohydrate constituents of wood are converted into lignin. These considerations seem to be amplified by the detection[20] of vanillin in wood decayed by the mold *Auricularia mesenterica*.

Acknowledgments.—The wood samples used in these investigations were obtained through the courtesy of Dr. L. C. Swain, of the Department of Forestry of the University, Durham, N. H.; the mold cultures from Dr. W. J. Robbins of the New York Botanical Garden; and "Indulin" from Dr. F. J. Ball of the West Virginia Pulp and Paper Co., Charleston, S. C.—This study was carried out under the auspices of the Office of Naval Research.

Summary

1. The net effect of the action of the wood-destroying fungi, *Lentinus lepideus*, *Poria vaillantii* and *Lenzites sepiaria* on white Scots pine and white fir woods is a depletion in the cellulose composition of the wood, together with a concomitant increase in the relative content of lignin.

2. After seven months of decay by *Lentinus lepideus* there is approximately a two-fold increase in the yield of alcohol-extractable lignin from the decayed wood in relation to that obtained from sound wood of the same species.

3. The native lignin of white Scots pine wood, and the lignin liberated from this wood by enzymatic degradation of the wood-cellulose appear to be identical.

4. Data are presented which indicate that native lignin is a chemical entity which is identical in various species of softwoods.

5. Lignin preparations isolated with 70% H_2SO_4, fuming HCl or 10% NaOH do not resemble native lignin in chemical composition nearly so closely as the lignin obtained after enzymatic decay of the wood.

6. A possible mechanism of lignification is discussed.

(20) O. Fernández and B. Regueiro, *Farm. nueva*, **11**, 223 (1946).

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[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY AND CHEMOTHERAPY, EXPERIMENTAL BIOLOGY AND MEDICINE INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

Some Reactions of the 2,4,6-Tribromophenyl β-D-Pyranosides of Glucose and Xylose

BY LEONORE H. KOEHLER AND C. S. HUDSON

Many years ago Fischer and Strauss[1] synthesized 2,4,6-tribromophenyl β-D-glucopyranoside (I) and observed that it decomposes in the presence of aqueous sodium or barium hydroxide, liberating tribromophenol. They were apparently of the opinion that D-glucose was formed concurrently. Present knowledge that phenyl β-D-glucopyranoside decomposes when treated drastically with aqueous potassium hydroxide solution, yielding phenol and levoglucosan,[2] has led us to restudy the behavior of tribromophenyl β-D-glucopyranoside; we find that when it is warmed with an aqueous solution of barium hydroxide it dissolves readily and is decomposed rapidly to give tribromophenol and levoglucosan (III) in high yield (78%). Its behavior is therefore like that of phenyl β-D-glucopyranoside but the reaction is a far more rapid one. The new 2,4,6-tribromophenyl β-D-xylopyranoside (IV), which cannot form a 1,6-anhydride of the type of levoglucosan, is decomposed by warm aqueous barium hydroxide solution to yield tribromophenol; the sugar moiety which is freed concurrently appears to suffer alkaline destruction since the solution soon develops much color.

Although phenyl β-D-glucopyranoside is not affected by refluxing with methanol containing sodium methoxide, tribromophenyl β-D-glucopyranoside dissolved slowly but completely at room temperature in this reagent in the course of two or three days, and from the solution methyl β-D-glucopyranoside (II), levoglucosan (III) (as triacetate) and tribromophenol could be isolated in yields of 21, 75 and 100%, respectively. No methyl α-D-glucopyranoside was detected. The tribromophenyl β-D-xylopyranoside (IV) reacts with methanolic sodium methoxide much more rapidly, doubtless because it is more soluble in the reagent; solution was complete at room temperature in thirty-five minutes with only a slight development of color, and methyl β-D-xylopyrano-

(1) E. Fischer and H. Strauss, *Ber.*, **45**, 2467 (1912).

(2) Edna M. Montgomery, N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **65**, 3 (1943).