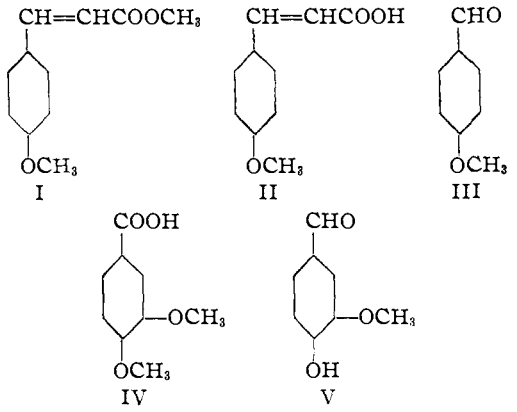


The enzymatic formation from carbohydrate of a methoxylated aromatic compound thus provides an insight into the mechanism whereby the carbohydrate constituents of wood are converted into lignin. These considerations seem to be amplified by the detection[20] of vanillin in wood decayed by the mold *Auricularia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

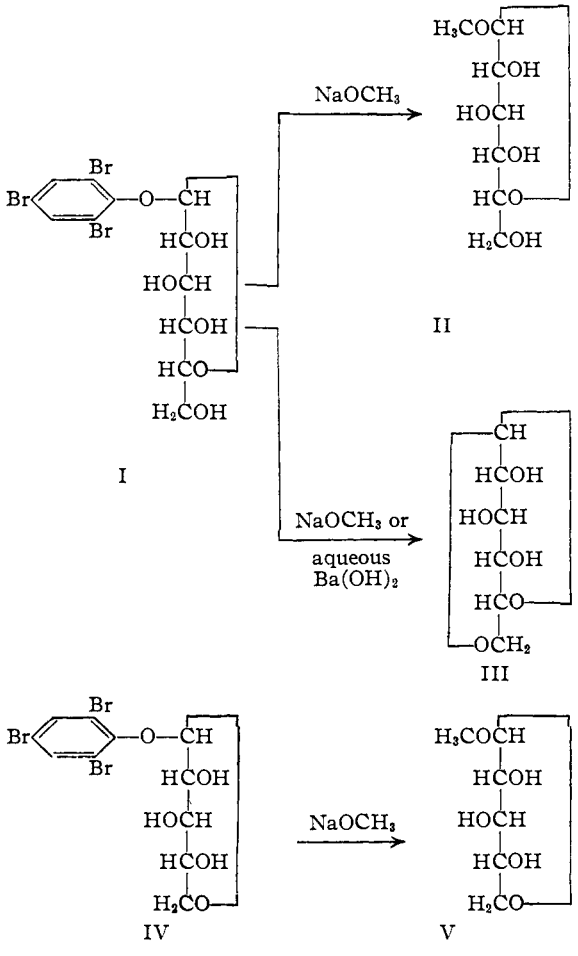
(1) E. Fischer and H. Strauss, *Ber.*, **45**, 2467 (1912).

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

side (V) and tribromophenol could be isolated in yields of 96 and 98%, respectively.

The β-D-configuration and the pyranose ring may be assigned to the tribromophenyl D-glucoside because of its hydrolysis by emulsin[1] and its mode of synthesis. The same β-D configuration and pyranose ring are assigned to the tribromophenyl xyloside because of its like mode of synthesis. The reactions that are illustrated by the formulas I to V have resulted in each case in the over-all retention of configuration for the anomeric carbon atom 1, but it is recognized that this retention may be the result of two Walden inversions, involving some intermediate that did not appear among the final products of the reactions. It is also recognized that the behavior of the tribromophenyl α-D-glucopyranoside and α-D-xylopyranoside, substances now unknown, should be studied in order to throw further light upon the mechanism of these reactions.

One of the authors (L. H. K.) thanks the Corn Industries Research Foundation for the fellowship under which the research was performed.




## Experimental

**2,4,6-Tribromophenyl β-D-Glucopyranoside Tetraacetate.**—A solution of β-D-glucopyranosyl bromide in dry chloroform, prepared from 50 g. of β-D-glucose pentaacetate by standard procedure, was mixed with 60 ml. of 1.25 *N* methanolic potassium hydroxide containing 33 g. of 2,4,6-tribromophenol, representing 1.25 mole equivalents of each of the latter substances. The clear yellow mixture stood sixty minutes at room temperature and was then refluxed for ninety minutes. A copious deposit of crystals of potassium bromide formed. The cooled mixture was washed with saturated sodium bicarbonate solution, followed by water washing, drying with calcium chloride and removal of solvent by distillation. At a volume of about 40 ml., when crystals began to appear, 60 ml. of hot absolute alcohol was added and solution completed by warming. The crystals of 2,4,6-tribromophenyl β-D-glucopyranoside tetraacetate which formed on cooling were nearly pure and the yield was 79% based on the glucose pentaacetate used. Recrystallization from alcohol yielded the pure substance, of m. p. 193–194°, as reported by Fischer and Strauss.[1]

**2,4,6-Tribromophenyl β-D-Glucopyranoside** (I).—Fischer and Strauss[1] reported that the tetraacetate of this glucoside split off tribromophenol when deacetylation by alkali or barium hydroxide was attempted and they overcame this difficulty by deacetylating with liquid ammonia at room temperature in a sealed tube. We find that the same result can be obtained by the use of methanol saturated with ammonia gas, which is a more convenient procedure. Ten grams of the tetraacetate was shaken at room temperature with 100 ml. of dry methanol which had been saturated with ammonia gas; solution was complete in eighty-five minutes. After two more hours most of the solvent was removed by aeration, leaving a pasty mass of white crystals which were washed with water, in which the glucoside is nearly insoluble. It was recrystallized from five parts of methyl cellosolve, forming platelets of m. p. 206° (cor.) and $[\alpha]_D$ −24.4° (*c*, 1.5 in pyridine), in agreement with the data of Fischer and Strauss.[1]

**Reaction of 2,4,6-Tribromophenyl β-D-Glucopyranoside with Sodium Methoxide.**—Dry methanol was prepared through customary distillation from magnesium ribbon. A suspension of 5 g. of the glucoside in 100 ml. of methanol in which 0.462 g. of sodium (2 mole equivalents) had been dissolved previously was shaken occasionally at room temperature (24°); solution was complete in fifty-two hours with no development of color. The solvent was removed, the white crystalline residue was dissolved in water and acidified with sulfuric acid to precipitate tribromophenol (3.3 g., quantitative). The filtrate was strongly levorotatory and its value indicated the presence of much levoglucosan. It was made slightly alkaline and then concentrated to a dry sirup which was taken up in 25 ml. of a potassium acetate solution made by dissolving 3 g. of potassium hydroxide in 100 ml. of absolute methanol and neutralizing with glacial acetic acid. Seeding with the molecular compound of potassium acetate and methyl β-D-glucopyranoside[3] and standing five days in the refrigerator gave a yield of the compound that corresponded to a 21% yield of methyl β-D-glucopyranoside. The mother liquor was concentrated to dryness and acetylated with acetic anhydride, the potassium acetate acting as catalyst. Levoglucosan triacetate of the correct m. p. and rotation was isolated in the usual way and indicated a yield of about 75% levoglucosan. The reaction thus produced about 75% levoglucosan, 21% methyl β-D-glucopyranoside, no methyl α-D-glucopyranoside and 100% tribromophenol.

**Reaction of 2,4,6-Tribromophenyl β-D-Glucopyranoside with Aqueous Barium Hydroxide.**—Five grams of the glucoside was warmed on the steam-bath with 200 ml. of water containing 3.1 g. of barium hydroxide octahydrate; solution was complete in thirty minutes and the color was slightly yellow. After ninety minutes longer on the bath, the solution was cooled and the barium was precipitated as sulfate along with tribromophenol. Extraction with ether yielded 3.30 g. of tribromophenol (98%). A yield

(3) A. J. Watters, R. C. Hockett and C. S. Hudson, THIS JOURNAL, **56**, 2199 (1934).

of 78% of pure crystalline levoglucosan was isolated from the aqueous filtrate by usual manipulations.

**2,4,6-Tribromophenyl β-D-Xylopyranoside Triacetate.**—It was prepared by the procedure used for its glucose analog and the yield was 75%. After recrystallization from three parts of ethanol, the substance melted at 129–131° and showed $[\alpha]^{20}D$ −66° (*c*, 0.8 in chloroform).

*Anal.* Calcd. for $C_{17}H_{17}O_8Br_3$: C, 34.66; H, 2.89. Found: C, 34.80; H, 2.93.

**2,4,6-Tribromophenyl β-D-Xyloside (IV).**—Deacetylation of the triacetate with ammoniacal methanol resulted in a nearly quantitative yield of the free xyloside. When recrystallized twice from forty parts of ethanol, the substance formed large prisms of m. p. 182–183° and showed $[\alpha]^{20}D$ −57° (*c*, 0.8 in pyridine).

*Anal.* Calcd. for $C_{11}H_{11}O_5Br_3$: C, 28.54; H, 2.40. Found: C, 28.68; H, 2.49.

**Reaction of 2,4,6-Tribromophenyl β-D-Xylopyranoside with Sodium Methoxide.**—Treated as has been described in the case of the glucose analog, 5 g. of this xyloside gave tribromophenol in 98% yield and methyl β-D-xylopyranoside in 96% yield, identified by its m. p., mixed m. p., crystalline habit (prisms) and specific rotation, ($[\alpha]^{20}D$ −63.3° in water).


## Summary

Fischer and Strauss[1] found that tribromophenyl β-D-glucopyranoside is very labile in alkaline solution, splitting off tribromophenol and, in their opinion, generating D-glucose. Present study of the glucoside shows that levoglucosan rather than D-glucose is formed in high yield in aqueous barium hydroxide solution. The reaction of the glucoside in methanol solution with sodium methoxide produces tribromophenol (100%), methyl β-D-glucopyranoside (21%) and levoglucosan (75%), with retention of configuration for both carbohydrates. Tribromophenyl β-D-xyloside yields similarly methyl β-D-xylopyranoside (96%) and tribromophenol (98%); in aqueous barium hydroxide the aryl xyloside yields tribromophenol; apparently the xylose moiety suffers alkaline decomposition since the solution soon develops much color.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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Synthesis of Bicyclo[4.2.0]octane-7,8-diol, A Derivative of "Cyclooctatetraene Dichloride"[1]

BY ARTHUR C. COPE AND ELBERT C. HERRICK

One of the reactions of cyclooctatetraene which is reported to proceed with rearrangement and yield a derivative of bicyclo[4.2.0]octane is the addition of chlorine.[2] Part of the evidence supporting this conclusion consisted in conversion of the dichloride to a diacetate, which was converted to bicyclo[4.2.0]octane-7,8-diol (III, whether *cis* or *trans* was not determined) by hydrogenation followed by hydrolysis. The structure of III was established by oxidation to *cis*-hexahydrophthalic acid, and cleavage with lead tetraacetate to *cis*-hexahydrophthalaldehyde.

Relatively few syntheses of bicyclo[4.2.0]-octane derivatives have been reported, and none by routes which appeared to be useful for a synthesis of III which would confirm its structure and furnish direct evidence for the presence of a cyclobutane ring in the molecule. We have investigated a relatively direct synthesis, consisting of the acyloin condensation of *cis*-diethyl hexahydrophthalate (I) to bicyclo[4.2.0]octan-7-ol-8-one (II), followed by catalytic hydrogenation of II to III.

The application of the acyloin condensation to the synthesis of cyclic acyloins containing large rings has been investigated thoroughly. The reaction conditions used by Hansley[3] for the preparation of acyclic acyloins were later applied to the synthesis of cyclic acyloins with a ring size of seven or more carbon atoms.[4] Prelog, Frenkiel, Kobelt and Barman,[5] and Stoll, Hulstkamp and Rouvé[6] have used similar reaction conditions very successfully for the preparation of cyclic acyloins with rings containing nine to twenty carbon atoms. The acyloin condensation does not appear to have been used for the closure of four-membered rings.

*cis*-Diethyl hexahydrophthalate (I) was prepared conveniently by the addition of butadiene to maleic anhydride to give *cis*-$\Delta^4$-tetrahydrophthalic anhydride, followed by esterification to *cis*-diethyl-$\Delta^4$-tetrahydrophthalate and catalytic hydrogenation to (I). Under conditions previously used for the synthesis of cyclic acyloins,[4,5,6] by slow addition of the ester (I) to four equivalents of sodium in refluxing xylene with high-speed stirring, a product was obtained which consisted largely of a polymer and the recovered ester (I). The ester appeared to contain some of the acyloin, however, for it absorbed a small amount of hydrogen on catalytic reduction, and after saponification to remove the ester, small amounts of a liquid with the properties of a glycol were isolated. By modifying the conditions of

(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96. Presented at the Atlantic City meeting of the American Chemical Society, Division of Organic Chemistry, September 20, 1949.

(2) Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

(3) Hansley, THIS JOURNAL, **57**, 2303 (1935).

(4) Hansley, U. S. Patent 2,228,268 (Jan. 14, 1941); *C. A.*, **35**, 2534 (1941).

(5) Prelog, Frenkiel, Kobelt and Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

(6) Stoll and Hulstkamp, *ibid.*, **30**, 1815 (1947); Stoll and Rouvé, *ibid.*, **30**, 1822 (1947).