

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Hydrolytic Derivatives of Lignin Volatile Compounds

BY A. BAILEY

The observation that acid hydrolysis of butanol lignin caused profound changes in the reaction mixture led to a closer examination of the products in the hope that they would have constitutional value. Acid hydrolysis of lignin is known to reduce methoxyl content, produce formaldehyde, and to cause deep-seated and unknown changes in the lignin, but little is known of the exact nature of the reaction.

Acid hydrolysis of butanol lignin yielded 27.5% of volatile compounds, a non-volatile, benzene-soluble fraction, and a resinous, alkali-soluble fraction. The volatile compounds are the only products discussed in this report. They were separated by careful fractionation in efficient columns and identified. The compounds and yields obtained were

Acetone, %	1.9
<i>n</i> -Butyraldehyde, %	1.6
Methanol, %	2.5
Allyl alcohol, %	2.5
Propyl alcohol, %	4.8
Formic acid, %	11.4
β -Ethyl- α -methylacrolein, %	2.8
	<hr/> 27.5

It seems probable that the 1.6% of *n*-butyraldehyde should be considered as derived from the butyl alcohol used as a solvent rather than from the lignin.

The methoxyl content of the original lignin was 15.2%; practically all of this was split off by hydrolysis, yet only 2.5% appeared as methyl alcohol. The abnormally high yield of the formyl radical may represent an oxidation product of the methanol formed by hydrolysis of the methoxyl group. It is to be noted that the sum of the yield of methanol and formic acid approached the original methoxyl content. This explanation, therefore, neither confirms nor invalidates Freudenberg's hypothesis that lignin contains the methylene dioxide group.

It is believed especially significant that three of the compounds possessed a carbon chain of three carbon atoms, two of them the allyl group and the other the propyl group. There would appear to be a close relationship between the allyl group

isolated here and that depicted by Klason,¹ and the propyl and allyl groups identified in this study with the hydrogenation products of Harris, D'Ianni and Adkins.²

The absence of aromatic compounds is undoubtedly due to non-volatility; it seems reasonable to expect them in the non-volatile, benzene-soluble fraction.

Butanol lignin from only three woods, western hemlock, aspen, and jack pine, has been subjected to acid hydrolysis but it has been ascertained that little similarity exists in the products of lignin from different species.

Hydrolysis with water and acid alone failed; the presence of butanol was necessary. A blank hydrolysis of water, hydrochloric acid, and butanol failed to yield butyl chloride or any other product.

Carbohydrates were not present in the reaction mixture, hence butanol lignin from hemlock is not a ligno-carbohydrate complex.

It is unfortunate that the use of butanol as a solvent precluded a determination of the quantity of butanol bound to the lignin in "butanol lignin" although time may show the other information presented here to be even more important.

The proven heterogeneity of butanol lignin³ is doubtless significant in relation to the number of products obtained.

In view of the diversity of products, the low yield, and the remaining products to be identified, it does not yet appear to be rational to hypothesize linkages which would fit the identified compounds into a constitutional scheme.

Experimental

Preparation of Lignin.—Western hemlock (*Tsuga heterophylla* Sargent) chips from a commercial sulfite chipper were digested in equal volumes of water and *n*-butanol in a 25-liter stainless steel rotating autoclave at 160°. Repeated digestions with fresh liquor were carried out to ensure removal of all free⁴ lignin. The lignin solution was then shaken with water until carbohydrates were removed, and concentrated to dryness.

Hydrolysis of Lignin.—One hundred grams of lignin, 550 ml. of distilled water, 550 ml. of butanol, and 24.4 ml.

(1) P. Klason, *Ber.*, **64**, 2733 (1931).

(2) E. E. Harris, J. D'Ianni and H. Adkins, *THIS JOURNAL*, **60**, 1467 (1938).

(3) A. Bailey, *Paper Trade J.*, **111**, TS73, Aug. 15 (1940).

(4) A. Bailey, *ibid.*, **110**, TS1-6, Jan. 4 (1940).

of 12 *N* hydrochloric acid were added to a 2-liter stainless steel autoclave, and digested at 160° for three hours. Two hydrolyses were carried out and the liquors combined before analysis.

Fractionation of Products.—Efficient columns were developed for this and similar studies; one of these has been described in detail.⁵ An extremely satisfactory method of fractionation involved the preliminary concentration of the reaction mixture by removal of the solvent. Two distillations in a column having an efficiency equivalent to 30 theoretical plates sufficed for concentration. The entire reaction mixture was then distilled through a 30-plate column, and the distillate added to the pot of another 30-plate column. The distillate from the second column was placed in the pot of a 60-plate column.⁵ These three columns were run simultaneously in this cascade system, keeping the volume of liquid in the higher pots at a minimum to increase the efficiency of separation. The technique of fractionation was generally similar to that already described.⁵

Yields were determined by the weight of distillate and the elimination curve.⁵

Identification of Products

(1) **Acetone.**—The 2,4-dinitrophenylhydrazone had a melting point of 125°. The semicarbazone melted at 185–186°, and the mixed melting point determination with acetone semicarbazone was 185°.

(2) ***n*-Butyraldehyde.**—The 2,4-dinitrophenylhydrazone melted at 120–121°, and the semicarbazone at 105°.

(3) **Methanol.**—The *p*-nitrobenzoate melted at 107°, and the 3,5-dinitrobenzoate at 107°.

(5) A. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **13**, 487 (1941).

(4) **Allyl Alcohol.**—The 3,5-dinitrobenzoate melted at 49°, and the *p*-nitrobenzoate at 28°.

(5) **Propyl Alcohol.**—The 3,5-dinitrobenzoate melted at 73–74° and the *p*-nitrobenzoate at 35°.

(6) **Formic Acid.**—The formyl radical occurred in the distillate as *n*-butyl formate, and the weight obtained is reported as formic acid. Actually, the *n*-butyl formate was isolated as the binary azeotrope, *n*-butyl formate–*n*-butanol, boiling at 105.8°. The butanol was removed from the mixture as the addition product of calcium chloride, and the residual butyl formate hydrolyzed by refluxing with 25% sodium hydroxide for one-half hour. The *n*-butanol was then distilled off as the binary azeotrope with water boiling at 92.7°, and salted out with potassium carbonate. The residual contents of the distillation flask were cooled, acidified and distilled. The formic acid was recovered as the binary water azeotrope; b. p. 107°.

The *n*-butanol was identified by preparing the 3,5-dinitrobenzoate, m. p. 62–63°, and *p*-nitrobenzoate, m. p. 35°.

The formic acid was identified by preparing the *p*-nitrobenzyl and the *p*-bromophenacyl esters. The *p*-nitrobenzyl ester had a melting point of 30–31°; the *p*-bromophenacyl ester, 138°.

(7) **β -Ethyl- α -methylacrolein.**—The 2,4-dinitrophenylhydrazone melted at 160°, the semicarbazone at 205°.

All of the above products were checked by identification with literature citation, melting points, or by mixed melting point determination.

Summary

Six aliphatic compounds, representing a yield of 25.7%, were identified in the acid hydrolyzate of butanol lignin.

SEATTLE, WASHINGTON

RECEIVED SEPTEMBER 4, 1941

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

The β -Form of the Cori Ester (*d*-Glucopyranose 1-Phosphate)

BY M. L. WOLFROM, C. S. SMITH, D. E. PLETCHER AND A. E. BROWN

Of all the biologically important sugar phosphates occurring in nature, the Cori ester (*d*-glucopyranose 1-phosphate) is perhaps of prime importance because of its role in the initial reactions of carbohydrate metabolism. The enzymatic synthesis of starch¹ and of glycogen² from this compound is indicative of its further significance. In a rigorous proof of structure of this substance reported from this Laboratory,³ no definitive α , β -assignment could be made since the corresponding α , β -isomer was unknown. The rather high dextrorotation (+78.5°) exhibited by the crystalline

dipotassium salt of the Cori ester does not in itself allow an α -assignment to be made. For example, β -*d*-galactose (+52°) and β -maltose (+118°) show high dextrorotations, but their corresponding α -isomers possess still greater rotations in the dextro direction. Accordingly, we sought a synthetic method of preparation for the second α , β -form.

Cori, Colowick and Cori⁴ state in a footnote that an attempt was made to prepare the α , β -isomer of the Cori ester by the interaction of β -acetochloroglucose and silver phosphate. Using an alkaline deacetylation procedure, they state that in one case they obtained an acid-labile bar-

(1) C. S. Hanes, *Proc. Roy. Soc. (London)*, **B129**, 174 (1940).

(2) R. S. Bear and C. F. Cori, *J. Biol. Chem.*, **140**, 111 (1941); cf. ref. 3 for previous citations.

(3) M. L. Wolfrom and D. E. Pletcher, *THIS JOURNAL*, **63**, 1050 (1941).

(4) C. F. Cori, S. P. Colowick and Gerty T. Cori, *J. Biol. Chem.*, **121**, 470 (1937).