allo-ocimene, anthracene, furan, sylvane, 2,5-dimethylfuran, furfuryl acetate and ergosterol. Mesacononitrile has been similarly condensed with cyclopentadiene. The resultant compounds have been characterized.

DAYTON, OHIO RECEIVED OCTOBER 25, 1946

[CONTRIBUTION FROM THE GRADUATE SCHOOL, UNIVERSITY OF WASHINGTON]

High-Boiling Hydrolytic Derivatives of Lignin

BY A. BAILEY

A previous publication[1] described the hydrolysis of butanol lignin in 50% aqueous butanol, about 0.25 *N* with hydrochloric acid, at 160° for three hours. Products boiling below butanol, arbitrarily designated as volatile products, were isolated in the following yields

	Yield, %		Yield, %
Methanol	2.5	Allyl alcohol	2.5
Formic acid	11.4	*n*-Butyraldehyde	1.6
Acetone	1.9	β-Ethyl-α-methyl-acrolein	2.8
Propylalcohol	4.8		
		Total	27.5

The present study was undertaken to ascertain the nature and yields of additional less volatile substances found in the acidic hydrolysis of lignin from western hemlock.

Procedure.—The source and preparation of the lignin, the hydrolysis, and the fractionation were described in a previous publication.[1] The present study has required, in addition, the use of appropriate high-vacuum pumps and stills. The least volatile products were collected in a molecular still of the Washburn type at a pressure of 10^{-6} mm. of mercury, measured by a McLeod gage.

Results.—The following additional "high-boiling" substances were obtained

	Yield, %		Yield, %
Resorcinol monomethyl ether	7.3	*n*-Butyric acid	1.0
m-Cresol	6.7	Guaiacol	0.3
		Vanillin	0.2
		Total	15.5

In addition to these compounds, 0.6% of complex phenols was obtained but the quantity was not adequate for characterization. A resinous, alkali-soluble fraction was also obtained.

Identification.—(1) **Resorcinol Monomethyl Ether.**—The N-α-naphthylcarbamate melted at 127–128° and the aryloxyacetic acid at 115–116°.

(2) *m*-**Cresol.**—The 3,5-dinitrobenzoate melted at 164°, mixed melting point of unknown and authentic sample of *m*-cresol showed no depression, and N-α-naphthylcarbamate melted at 125–126°.

(3) *n*-**Butyric Acid.**—The S-benzylthiuronium salt melted at 144° and the *p*-phenylphenacyl ester at 80–80.3°.

(4) **Guaiacol.**—The *p*-nitrobenzoate melted at 90–90.5° and the 3,5-dinitrobenzoate, crystallized from alcohol, at 140–140.4°.

(5) **Vanillin.**—The oxime melted at 115–115.7° and the 2,4-dinitrophenylhydrazone (from acetic acid) at 269°.

Discussion.—The total yield of products is of the same order as was obtained by Hibbert and co-workers in the hydrolysis of maple lignin in the presence of ethanol and hydrogen chloride, although the structures of the compounds obtained show less relationship. While benzene rings and short aliphatic chains have been found in both studies, Hibbert found them combined in compounds having the carbon skeleton of propyl benzene. This carbon skeleton has not been found in the present study although propyl compounds and benzene derivatives have been found. Hibbert used maple lignin while western hemlock lignin was used in these experiments.

The appearance of methoxyl in a resorcinol derivative was unexpected and suggests the presence of a structure of the meta configuration in the native lignin rather than the more common 1,2-substituted compounds such as guaiacol, the 1,3,4-substituted compounds such as vanillin, and the 1,4-substituted hydrogenation derivatives. The original methoxy appears to be satisfactorily accounted for in the yield of methanol, formic acid and resorcinol monomethyl ether. The occurrence of *m*-cresol in substantial quantities likewise suggests that the 1,3-substituted benzene nucleus should be considered in relation to constitution.

It is possible that the *n*-butyric acid should be regarded as derived from the butanol solvent rather than from the lignin.

Constitutional conclusions that might tentatively be drawn from the above experiments are these: hydrolysis (and perhaps mild oxidation as well) converts 40% of the lignin into identifiable compounds. About one-third are phenolic, and the remaining two-thirds are short-chain, aliphatic compounds. There is general similarity between these products and previously isolated derivatives of lignin. In view of the many products of reaction, and the 60% fraction of the lignin not converted to identifiable products, it does not appear justified to propose a constitutional model from the data of these experiments.

While the original intent was to learn the effects of acidic hydrolysis, the nature of the compounds identified suggests that mild oxidation also occurred.

The discussion in the previous paper,[1] relating to the more volatile products identified, does not appear to be in need of correction ir the light of

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[1] A. Bailey, THIS JOURNAL, **64**, 22 (1942).

this later investigation and should be consulted for further comments.

Summary

Five compounds were identified as high-boiling hydrolytic derivatives of lignin, in a yield of 15.5%. Together with the six low-boiling compounds in 27.5% yield, reported in an earlier publication, the total yield of the reaction came to 43.3%. The compounds identified were generally similar to known derivatives of lignin preparations. The experimental data were not considered adequate to support the proposal of a constitutional model.

SEATTLE, WASHINGTON RECEIVED NOVEMBER 18, 1946

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE LAKESIDE LABORATORIES, INC.]

The Base Effect in Catalytic Hydrogenation. A Simple Synthesis of 6-Methoxy-α-tetralone

BY GILBERT STORK[1]

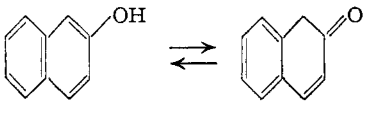
In an attempted preparation of β-tetralone by the catalytic hydrogenation of β-naphthol[1a] with Raney nickel a tetralol fraction was obtained which solidified and was found to consist mostly of the *phenolic ar*-tetrahydro-β-naphthol. This result could not be reconciled with that of previous investigators who had studied the catalytic hydrogenation of β-naphthol to its tetrahydro derivative, using nickel or Raney nickel catalysts, and who had reported the product of the reaction to be the non-phenolic *ac*-tetrahydro-β-naphthol.[2] Only one of these workers[2c] had reported the simultaneous formation of approximately equal amounts of both isomers.

This lack of agreement prompted us to reinvestigate the catalytic hydrogenation of β-naphthol with Raney nickel. It was found that, contrary to the results previously reported with this catalyst,[2d,e,f] the absorption of two moles of hydrogen per mole of β-naphthol brings about the preferential saturation of the non-phenolic ring with the formation of the *phenolic ar*-tetrahydro-β-naphthol. Some of the isomeric *ac*-tetrahydro-β-naphthol is also formed, a typical yield being 66% of 5,6,7,8-tetrahydro-β-naphthol and 33% of the non-phenolic isomer.[3] The two compounds can easily be separated by extraction of the *ar*-tetrahydro-β-naphthol with very dilute (2%) sodium hydroxide solution. More concentrated solutions fail to dissolve the sodium salt. Once separated, the two isomers can be readily differentiated by comparing their behavior toward diazotized aromatic amines.

The finding that β-naphthol is reduced preferentially in the unsubstituted ring throws some doubt on Palfray's conclusion[2f] that a hydroxyl group facilitates the reduction of an aromatic ring. It is suggested that in a polycyclic aromatic compound that ring will become reduced, the reduction of which will result in the smallest loss of resonance energy by the system. If this be so, then one would expect that in a system like naphthalene almost any substituent introduced in one ring will stabilize that ring toward hydrogenation, and the normal product of the Raney nickel hydrogenation of β-naphthol would then be expected to be *ar*-tetrahydro-β-naphthol, as was indeed found.

It should be pointed out, however, that this conclusion will be valid only in the absence of other factors which under the proper conditions may well play a determining part in directing the hydrogenation. For instance, it would not be expected that the presence of acid in the reduction medium would materially affect the course of the reduction of β-naphthol since this would cause little change in the molecule undergoing reduction. In the presence of some diethylamine hydrochloride or acetic acid in the alcohol solution the hydrogenation was somewhat slower than in a neutral medium, but the products from these reductions were qualitatively similar to those obtained without acid, and the main constituent was again the phenolic 5,6,7,8-tetrahydro-β-naphthol.

In the presence of added base, however, the situation is quite different. In the first place, the phenolic moiety will be more strongly adsorbed on the basic catalyst than the rest of the molecule, and secondly it will have the possibility of tautomerizing to the non-aromatic α,β-unsaturated ketone system



As a matter of fact, when the catalytic hydrogenation of β-naphthol was conducted in the

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(1) Present address: Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts.

(1a) Stork and Foreman, THIS JOURNAL, **68**, 2172 (1946).

(2) (a) Schroeter, Svanoe, Einbeck, Geller and Riebensahm, *Ann.*, **426**, 83 (1921); (b) Brochet and Cornubert, *Bull. soc. chim.*, **31**, 1280 (1922); (c) Kimura, *J. Chem. Soc. Japan*, **51**, 208 (1930); *C. A.*, **26**, 720 (1932); (d) Musser and Adkins, THIS JOURNAL, **60**, 664 (1938); (e) Palfray, *Compt. rend.*, **206**, 1976 (1938); (f) Palfray, *Bull. soc. chim.*, [5] **7**, 407 (1940).

(3) Professor Homer Adkins has told us that H. P. Schultz, working in his laboratory, had observed the formation of the phenolic 5,6,7,8-tetrahydro-β-naphthol in a Raney nickel hydrogenation of β-naphthol.