

acetone gave the analytical sample (85% yield) of the diol Va with m.p. 177–179°, $[\alpha]_D^{20} -51^\circ$, no selective absorption in the ultraviolet between 216–300 m μ .

Anal. Calcd. for C₂₂H₃₄O₂: C, 79.95; H, 10.37. Found: C, 79.75; H, 10.23.

The diacetate Vb (acetic anhydride–pyridine, one hour, steam-bath) was isolated as colorless crystals with m.p. 180–182°, $[\alpha]_D^{20} -28^\circ$ after recrystallization from methanol.

Anal. Calcd. for C₂₆H₃₈O₄: C, 75.32; H, 9.24. Found: C, 75.18; H, 8.98.

16,17-Methyleneprogesterone (VI).—A solution of 5.0 g. of Δ^5 -16,17-methylenepregnen-3 β -ol-20-one (IVa) and 10 g. of aluminum *t*-butoxide in 100 cc. of toluene and 50 cc. of cyclohexanone was refluxed for one hour and then steam distilled. The residue was extracted with ether, washed with a saturated solution of Rochelle salt, dried and evaporated. Crystallization from ethyl acetate gave 3.9 g. of crystals with m.p. 180–187°. The analytical sample of the ketone VI crystallized as long, colorless prisms with m.p. 191–192°, $[\alpha]_D^{20} +211^\circ$, ultraviolet maximum at 240 m μ (log ϵ 4.32). A sample was sublimed under high vacuum at 130° before analysis.

Anal. Calcd. for C₂₂H₃₀O₂: C, 80.93; H, 9.26. Found: C, 80.74; H, 9.29.

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The Citronellol Problem and the Isolation of α -Citronellol

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Despite continuing controversy^{1,2} it has been proved,^{3,4,5} and recently confirmed⁶ that natural citronellol is virtually free from α -citronellol (I), nature offering only β -citronellol (II). Pure α -citronellol has never been isolated, though Doeuivre^{7,8} reported that citronellol could be isomerized to a mixture containing about 30 to 50% of I. This conclusion was based only on ozonolyses, no significant changes in physical properties being detected. Naves⁹ also affirmed that "no physical difference, other than the Raman effect, has been demonstrated between citronellol (rhodinol) β -isomer and the mixtures of isomers."

I wish to report the isolation of I in approximately 95% purity by distillation. Citronellol (b.p. (10 mm.) 104.6°, $n_D^{25} 1.4540$, $d_4^{25} 0.8515$) from the reduction of citronellol, was obtained by fractional distillation (10 mm. pressure) in a 6-ft. Podbielniak column, and was saponified after heating with benzoyl chloride at 160° for 6 hours. The products were distilled using a reflux ratio of 100 and amongst others, a material of b.p. (10 mm.) 103.0°, $n_D^{25} 1.4501$ and $d_4^{25} 0.8488$ was obtained. This was followed by a long series of intermediate fractions leading to unchanged II. Redistillation of selected fractions yielded a purer product (A) of $n_D^{25} 1.4494$, $d_4^{25} 0.8484$ and $[\alpha]_D^{25} -1.63^\circ$. A reflux ratio of 40 was found to be insufficient to produce any worthwhile separation.

β -Citronellol and A differ only in the site of unsaturation, since catalytic hydrogenation of either yields dihydrocitronellol identified as the phenylazophenylurethan,⁹ m.p.

86.5–87.5°, clusters of orange plates from hexane (found: C, 72.7; H, 8.05). From the 73% yield of formaldehyde obtained from A by an oxidative procedure¹⁰ and from its optical activity it follows that A is mainly α -citronellol. The proportion of II in A was measured by the Kuhn and Roth¹¹ ozonization technique, yields of only 5–6% of acetone being obtained, whereas II gave 93–98% yields.

The phenylazophenylurethan (found: C, 72.9; H, 7.51) from A formed clusters of orange plates of m.p. 64–65° from hexane and yielded 3.1% and 4.8% of acetone. The urethan (found: C, 72.6; H, 7.62) from II formed clusters of orange plates of m.p. 69–70° from hexane and yielded 96 and 97% of acetone. A mixture of these urethans, ground together in equal proportions, melted at 64–69° but after fusing or crystallizing together from hexane, the melting point was 66–67.5° indicating that solid solutions are formed by these derivatives of I and II.

(10) Bricker and Roberts, *Anal. Chem.*, **21**, 1331 (1949).

(11) Kuhn and Roth, *Ber.*, **65**, 1285 (1932).

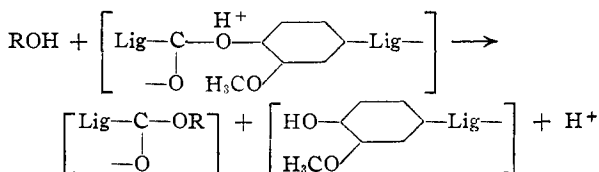
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Solubility Effects in Lignin Alcoholysis Reactions

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Evidence gained from studies on isolated ethanol lignins indicates that in the isolation of lignin with ethanol and hydrogen chloride changes occur which include introduction of ethoxyl groups,¹ depolymerization² and the liberation of phenolic groups.³ Making the as yet unproven but plausible assumptions, first that protolignin exists in a high polymeric form, and second that these three reactions are interrelated, one arrives at the conclusion that this isolation method may be an acid-catalyzed solvolytic cleavage of hydrophobic polymer or polymers in the presence of a suitable solvent.⁴ In its simplest form such an interpretation can be pictured schematically as follows (ignoring reaction mechanism)



and appears not to conflict with our present qualitative knowledge of the reactions of lignin with mercaptans, alcohols, phenols and perhaps carboxylic acids.⁵

Fortunately this speculation invites experimental verification or disproof by a variety of methods. As a first step in a more rigorous analysis, we choose to adopt the idea as a working hypothesis and to

(1) W. S. MacGregor, T. H. Evans and H. Hibbert, *THIS JOURNAL*, **66**, 41 (1944), and many earlier references.

(2) W. B. Hewson and H. Hibbert, *ibid.*, **65**, 1173 (1943), and earlier references.

(3) C. Schuerch, Jr., *ibid.*, **72**, 3838 (1950).

(4) This statement is not completely original, having been stated at least in part by previous workers and in part implied by the term alcoholysis. The author's debt can easily be traced in any of several published reviews and in references listed here.

(5) Similarly the sulfite process is now interpreted as the introduction of hydrophilic functional groups into the lignin complex and a subsequent acid-catalyzed hydrolytic cleavage of lignin-lignin or lignin-carbohydrate bonds. It is not surprising that variable percentages of phenolic groups and variable oxygen contents seem common in lignin sulfonic acid preparations. See H. Erdtman, B. O. Lindgren and T. Petterson, *Acta. Chem. Scand.*, **4**, 228 (1950).

(1) Owen and Simonsen, *Endeavour*, **8**, 26 (1949).

(2) Naves, *Perfumery Essent. Oil Record.*, **40**, 41 (1949).

(3) Doeuivre, *Bull. soc. chim.*, [5] **3**, 613 (1936).

(4) Naves, Brus and Allard, *Compt. rend.*, **200**, 1112 (1935).

(5) Carroll, *Perfumery Essent. Oil Record*, **38**, 226 (1947).

(6) Barnard, et al., *J. Chem. Soc.*, 915 (1950).

(7) Doeuivre, *Bull. soc. chim.*, [4] **45**, 351 (1929).

(8) Naves, *Perfumery Essent. Oil Record*, **37**, 120 (1946).

(9) Davenport and Sutherland, *Univ. Queensland, Papers, Dept. Chem.*, **1**, No. 39 (1950).

consider the solvent function of the solvent in such a reaction (ignoring its reactant function). Obviously if the solubility of the derived lignins is a limiting factor in the reaction, high yields will be obtained only with the better lignin solvents.⁶ A perusal of the literature suggest this to be the case. Fuchs reports nearly complete lignin removal with the excellent solvents phenol and "methoxyglycol,"⁷ while methanol⁸ and ethanol⁹ give only poor yields from the same wood. Increasing the quantity of ethanol increases the yield of ethanol lignin,¹⁰ as would be expected.

Experiments outlined in Fig. 1 are believed to separate largely the solvent and reactant effects of the solvent in a typical reaction. One-gram

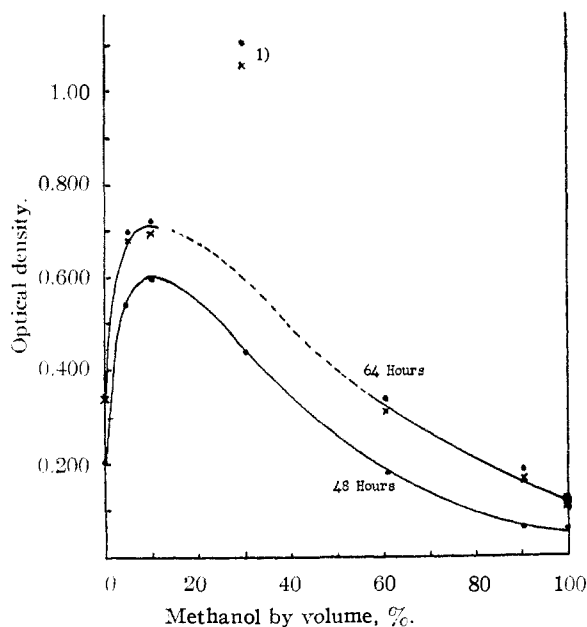


Fig. 1.—Lignin removal by alcoholysis in dioxane-methanol mixtures: ●, optical density of solution at 275 $m\mu$; x = at 280 $m\mu$; (1) values discarded, 64-hour run.

samples of dry alcohol- and ether-extracted spruce wood meal (100 mesh) were treated in sealed glass tubes at 60–62° with 15 ml. of solvent mixtures varying from pure dioxane to pure methanol,¹¹ all containing 2% hydrogen chloride. Runs were made for 48 and 64 hours. By means of a Beckman quartz spectrophotometer, the optical density of the various solutions (diluted 625 times with pure dioxane) at wave lengths 275 and 280 $m\mu$ was

(6) Fragments of larger molecular weight will also dissolve in quantity in the better solvents.

(7) W. Fuchs, *THIS JOURNAL*, **58**, 675 (1936).

(8) M. Phillips in Wise's "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 289.

(9) L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert, *THIS JOURNAL*, **61**, 868 (1939).

(10) W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3041 (1941).

(11) The methanol was a commercial anhydrous grade, the dioxane a purified grade refluxed with hydrochloric acid, dried over sodium hydroxide, and distilled from sodium; cf. Fieser's "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., 1941, p. 368. Customary but not extreme precautions were taken to ensure the absence of alcohols and water. The nature of the substrate and the complexity of the reaction tend to make absolute precision difficult to obtain and at present perhaps not too significant.

determined and was used as a semiquantitative measure of lignin removal.¹² With pure dioxane, the lignin removal was small, since functional groups suitable for reaction with the lignin are present only fortuitously in the solvent.¹³ On adding methanol, the yield of lignin increased to a maximum, which was greater than the sum of that formed in either pure solvent, and then decreased as the poor solvent power of the methanol limited the solubility of the product.

This observation is of obvious general application to lignin isolation procedures and indicates that the low reported yields of lignin alcoholysis products are mainly the result of the slight solubility of the products in the solvent rather than solely the result of polymerization reactions, as might be inferred from earlier work.¹⁰ It does not constitute proof of the original assumptions or of the absence of such polymerization reactions.

Acknowledgment.—The author is indebted to Mrs. M. Granath for the determinations of optical density reported herein.

(12) This method of analysis for lignin is arbitrary and subject to some obvious errors, as are all others. In view of the similarity of the systems used in these experiments, semiquantitative validity appears assured.

(13) Freudenberg claims no removal of lignin in the absence of alcohols, according to F. Brauns in Ott's "Cellulose and Cellulose Derivatives," Interscience Publishers, New York, N. Y., 1943, p. 454. Our results indicate the same trend.

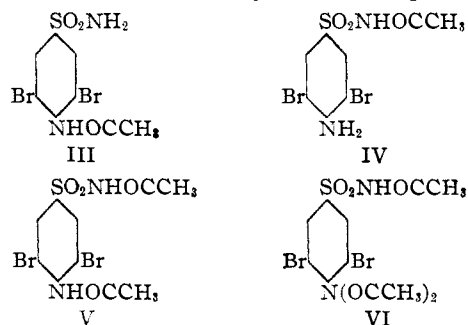
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Acetylation of 3,5-Dibromosulfanilamide

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In continuation of the work on halogenated derivatives of sulfanilamide,^{2,3,4} the acetyl derivatives of 3,5-dibromosulfanilamide (I) have been prepared. Like the analogous dichloro compound (II),⁴ I yields the four possible acetyl derivatives, III, IV,⁵ V and VI directly and under practically



identical conditions. Increases in the time required for complete acetylation in the preparation of IV, V and VI and a decrease for III represent the only significant differences.

The properties of III, IV, V and VI are also very

(1) Submitted in June, 1950, in partial fulfillment for the degree with honors.

(2) M. K. Seikel, *THIS JOURNAL*, **62**, 1214 (1940).

(3) M. K. Seikel, *Org. Syntheses*, **24**, 47 (1944).

(4) M. K. Seikel, *THIS JOURNAL*, **70**, 3344 (1948).

(5) Previously prepared by the bromination of N¹-acetylsulfanilamide, m.p. 193.8–194.6° (uncor.), by E. H. Wells, *J. Assoc. Official Agri. Chem.*, **25**, 747 (1942); *C. A.*, **36**, 6751 (1942).