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

Anal. Calcd. for $C_{22}H_{34}O_2$: 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°, $[\alpha]^{20}D$ −28° after recrystallization from methanol.

Anal. Calcd. for $C_{26}H_{38}O_4$: 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-3β-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°, $[\alpha]^{20}D$ +211°, ultraviolet maximum at 240 mμ (log ε 4.32). A sample was sublimed under high vacuum at 130° before analysis.

Anal. Calcd. for $C_{22}H_{30}O_2$: 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

BY MAURICE D. SUTHERLAND

Despite continuing controversy[1,2] it has been proved,[3,4,5] and recently confirmed[6] that natural citronellol is virtually free from α-citronellol (I), nature offering only β-citronellol (II). Pure α-citronellol has never been isolated, though Doeuvre[7,3] reported that citronellol could be isomerized to a mixture containing about 30 to 50% of 1. This conclusion was based only on ozonolyses, no significant changes in physical properties being detected. Naves[8] 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°, $n^{25}D$ 1.4540, d^{25}_4 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°, $n^{25}D$ 1.4501 and d^{25}_4 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 $n^{25}D$ 1.4494, d^{25}_4 0.8484 and $[\alpha]^{25}D$ −1.63°. 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 procedure[10] 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 Roth[11] 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.

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

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

[3] Doeuvre, *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] Doeuvre, *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).

[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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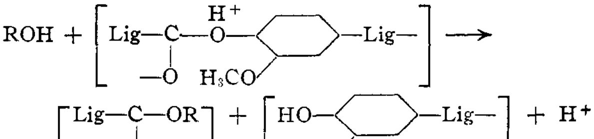
Evidence gained from studies on isolated ethanol lignins indicates that in the isolation of lignin with ethanol and hydrogen chloride changes occur which include introduction of ethoxyl groups,[1] depolymerization[2] and the liberation of phenolic groups.[3] Making the as yet unproven but plausible assumptions, 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

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[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).