902. *The Components of Wool Wax. Part I. The Aliphatic Alcohols.*

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Five alcohols have been isolated from the unsaponifiable fraction of wool wax and identified as *n*-octadecanol, *n*-eicosanol, *n*-docosanol, *n*-tetracosanol, and *n*-hexacosanol.

It has usually been assumed that the aliphatic alcohols obtained by hydrolysis of wool wax are members of the normal series, but this is inadequately substantiated. The presence of *n*-hexadecanol has been demonstrated by Drummond and Baker (*J. Soc. Chem. Ind.*, 1929, **48**, 232T) but substances such as carnaubyl and ceryl alcohols are undoubtedly mixtures (Truter, *Quart. Reviews*, 1951, **5**, 390). The melting points of these alcohols and their acetates are 5—10° lower than those of the corresponding *n*-compounds. Matthes and Sauder (*Arch. Pharm.*, 1908, **246**, 169) showed that "carnaubyl" alcohol, m. p. 68°, from laurel oil was a mixture of an alcohol of m. p. of 88° and a hydrocarbon of m. p. 69°, but a similar explanation is unlikely in the case of wool wax because its hydrocarbon content is estimated at less than 1% (Daniel, Lederer, and Velluz, *Bull. Soc. Chim. biol.*, 1945, **27**, 218).

That the aliphatic alcohols of wool wax may be of considerable complexity is illustrated by the facts that Kuwata and Katuno (*J. Soc. Chem. Ind. Japan, Suppl.*, 1938, **41**, 227) isolated an isomeric C_{18} alcohol, indicating that a series of branched-chain alcohols might be present, and Horn and Houghen (*Chem. and Ind.*, 1951, 670) isolated five long-chain 1 : 2-diols. We now record the separation and characterisation of the five even-numbered alcohols from *n*-octadecanol to *n*-hexacosanol (cf. *Chem. and Ind.*, 1951, 911), together with some evidence for a group of optically active alcohols.

A solution of commercial wool-wax alcohols ("Hartolan," Messrs. Croda, Ltd.) in benzene–chloroform was added to finely powdered urea which had been moistened with methanol. Within 3 weeks, about 19% of the alcohols formed an addition complex with urea. When the acetates of the alcohols recovered from the complex were treated three times with urea, about one-fifth of them did not form complexes. Such behaviour would be expected for 1 : 2-diols because of the conversion of an essentially straight-chain alcohol into a branched-chain ester (Truter, *J.*, 1951, 2416). By using the difference in affinity of members of a homologous series for urea, the complex was subjected to a 26-stage fractional crystallisation from constant-boiling ethanol–benzene.

The mixed acetates had a slight optical rotation which gradually became concentrated in the more soluble fractions, *i.e.*, those which had a low affinity for urea. The more insoluble fractions, in which the *n*-alcohols occurred, were inactive. That portion of the acetates which did not form a urea complex was hydrolysed and the free alcohols chromatographed on alumina. The fractions that were easily eluted with ether had a higher optical rotation than those more strongly adsorbed. Horn and Houghen (*loc. cit.*) state that the more strongly adsorbed diols are optically inactive. Hence, in addition to the *n*-alcohols and the diols, a third series of aliphatic alcohols must be present.

There was no evidence for the occurrence of *n*-alcohol higher than hexacosanol. Attempts to isolate *n*-hexadecanol and *n*-tetradecanol were unsuccessful because of the persistent optical activity of the lower fractions. *n*-Octadecanol, *n*-tetracosanol, and *n*-hexacosanol occur in approximately equal quantities; *n*-eicosanol is rather more abundant, and there is about twice as much *n*-docosanol. Altogether the *n*-alcohols amount to about 10% of the total, the diols to 4%, and the remaining optically active fractions to 4%.

EXPERIMENTAL

M. p.s are uncorrected. Microanalyses are by Mrs. Y. Richards (Leeds) and by Drs. Weiler and Strauss (Oxford).

Isolation of the Straight-chain Alcohols.—" Hartolan " (300 g.) was dissolved in benzene–chloroform (1 : 1; 1200 ml.) and the solution poured on finely powdered urea (450 g.) which had been moistened with methanol (90 ml.). After 19 days at room temperature with occasional stirring, the complex was filtered off and washed with solvent until the washings were a pale straw colour (*ca.* 500 ml.). The complex was dried and decomposed by water (1500 ml.), and the alcohols extracted with ether (750 ml.). The aqueous solution was again extracted with ether (250 ml.), and the combined extracts were washed with water (5 × 250 ml.), dried (Na_2SO_4), and evaporated, to yield material (56 g.) of m. p. 59·5—63·5°.

Removal of Secondary Alcohols.—The alcohols (56 g.) were refluxed with acetic anhydride (35 ml.) in pyridine (50 ml.) for 5 hours, the solution was then poured into water, the acetates were filtered off, and the residue was dissolved in light petroleum (250 ml.). The solution was washed with water (4 × 100 ml.), dried (Na_2SO_4), and decolorised with charcoal (5 g.) at the b. p. (2 mins.), giving acetates (51·5 g.), m. p. 39—42°, $[\alpha]_D^{20}$ +1·38° in $CHCl_3$. A solution of these in light petroleum (500 ml.) was poured on finely powdered urea (200 g.), moistened with methanol (40 ml.). After 48 hours the complex was filtered off, washed with light petroleum (3 × 100 ml.), dried, and decomposed by water (1 l.), and the esters were extracted with ether (2 × 250 ml.). The combined ethereal extracts were washed with water (3 × 200 ml.), dried (Na_2SO_4), and evaporated, giving alcohols (36 g.) of m. p. 39—46°, $[\alpha]_D^{20}$ +1·0° in $CHCl_3$. The light petroleum filtrate and washings were concentrated (400 ml.) and again allowed to react, for 24 hours, with urea (20 g.) moistened with methanol (4 ml.), yielding, after recovery as above, 1·3 g. of acetates. A third treatment with urea gave only 0·2 g. of acetates. The filtrate was washed with water (4 × 200 ml.) and dried (Na_2SO_4), and the solvent removed. The residue (11 g.), m. p. 22—27°, $[\alpha]_D^{20}$ +1·9° in $CHCl_3$, consisted mainly of *sec.*-alkyl acetates.

A mixture of the combined straight-chain acetates (78 g.) and urea (270 g.) was subjected to a 26-stage systematic fractional crystallisation from constant boiling ethanol–benzene.

Isolation of the Free Alcohols.—The acetate (0·5 g.) was hydrolysed by boiling alcoholic potassium hydroxide (25 ml.; 0·25N) and the sap. value determined by back-titration. The alcoholic solution was then diluted with N-aqueous potassium hydroxide (100 ml.), and the free alcohol extracted with ether (100 ml.). The extract was washed with aqueous alkali (4 × 50 ml.) (to remove the indicator), and then with water (3 × 50 ml.). The solution was dried (Na_2SO_4) and the ether distilled off.

C_{26}-*Fraction.*—The acetate, recrystallised three times from acetone, had m. p. 63·0° (Found : C, 79·1; H, 13·2%; sap. val., 131·3. Calc. for $C_{28}H_{56}O_2$: C, 79·2; H, 13·3%; sap. val., 132·2). After recrystallisation from acetone the alcohol had m. p. 77·5—80·0° (Found : C, 81·6; H, 14·1. Calc. for $C_{26}H_{54}O$: C, 81·6; H, 14·2%) [*α-naphthylurethane*, m. p. 89·3—90·0° (Found : N, 2·5. $C_{37}H_{61}O_2N$ requires N, 2·5%); phenylurethane, m. p. 88·7°].

C_{24}-*Fraction.*—The acetate, recrystallised twice from acetone, had m. p. 57·5° (Found : C, 78·9; H, 13·2%; sap. val., 141·3. Calc. for $C_{26}H_{52}O_2$: C, 78·7; H, 13·2%; sap. val., 141·0). The alcohol had m. p. 73·8—74·7° (Found : C, 81·4; H, 13·9. Calc. for $C_{24}H_{50}O$: C, 81·3; H, 14·2%) [*α-naphthylurethane*, m. p. 88·3—89·1° (Found : N, 3·0. $C_{35}H_{57}O_2N$ requires N, 2·7%); phenylurethane, m. p. 87·4°].

C_{22}-*Fraction.*—The acetate had m. p. 49—51° (Found : C, 78·4; H, 13·0%; sap. val., 151·8. Calc. for $C_{24}H_{48}O_2$: C, 78·2; H, 13·1%; sap. val., 152·3), and the alcohol, m. p. 69·4—69·9° (Found : C, 81·2; H, 14·3. Calc. for $C_{22}H_{46}O$: C, 80·9; H, 14·2%) [*α-naphthylurethane*, m. p. 86·9—87·1° (Found : N, 2·6. $C_{35}H_{53}O_2N$ requires N, 2·8%)]; *phenylurethane*, m. p. 85·7—86·2° (Found : N, 3·1. $C_{29}H_{51}O_2N$ requires N, 3·2%). The acid obtained by oxidation of the alcohol with chromic oxide in acetic acid had m. p. 78—80°.

C_{20}-*Fraction.*—The acetate had m. p. 41·1—42·0° (Found : C, 77·9; H, 13·0%; sap. val., 165·0. Calc. for $C_{22}H_{44}O_2$: C, 77·6; H, 13·0%; sap. val., 164·8), and the alcohol, m. p. 64·8—65·0° (Found : C, 80·5; H, 14·1. Calc. for $C_{20}H_{42}O$: C, 80·5; H, 14·2%) [*phenylurethane*, m. p. 84·5—85·6° (Found : N, 3·3. $C_{27}H_{47}O_2N$ requires N, 3·3%)].

C_{18}-*Fraction.*—The acetate had m. p. 31·5° (Found : C, 77·1; H, 13·0%; sap. val., 178·0.

Calc. for $C_{20}H_{40}O_2$: C, 76·9; H, 12·9%; sap. val., 179·5). The alcohol had m. p. 57·1—58·5° (Found: C, 79·8; H, 14·0. Calc. for $C_{18}H_{38}O$: C, 79·9; H, 14·2%) and the acid, m. p. 68·4—68·9° alone or mixed with octadecanoic acid (Found: C, 76·4; H, 12·5. Calc. for $C_{18}H_{36}O_2$: C, 76·0; H, 12·7%).

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