49. *The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part IX. The Structure of Batyl and Selachyl Alcohols.*

By W. H. Davies, I. M. Heilbron, and W. E. Jones.

As both synthetic α-octadecyl glyceryl ether (I) and its diphenylurethane give small but definite depressions in m. p. when admixed respectively with batyl alcohol and its diphenylurethane, Davies, Heilbron, and Owens (J., 1930, 2542) considered that the natural product was probably the isomeric β-octadecyl glyceryl ether (II)

(I.) $C_{18}H_{37}\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ $C_{18}H_{37}\cdot O\cdot CH(CH_2\cdot OH)_2$ (II.)

On the other hand, Knight (*Biochem. J.*, 1930, **24**, 257) from evidence provided by unimolecular film measurements concluded that batyl alcohol possessed the unsymmetrical α-structure (I), a finding strongly supported by Adam (see previous paper).

We have now obtained, in agreement with the latter author's views, conclusive proof of the presence of an αβ-glycol grouping in batyl alcohol by applying Criegee's elegant method of oxidation (*Ber.*, 1931, **64**, 260), formaldehyde (identified as its 2 : 4-dinitrophenylhydrazone) and *glycollaldehyde octadecyl ether* being produced. The structure of the latter aldehyde has been confirmed by its synthesis from octadecyl allyl ether (Davies, Heilbron, and Owens, *loc. cit.*) by the action of ozone. On oxidation with chromic anhydride the aldehyde readily yields the corresponding *glycollic acid octadecyl ether*, m. p. 62—63°. The above result shows that batyl alcohol can differ only in configuration from the synthetic α-octadecyl glyceryl ether, and in agreement with this we have now ascertained that the alcohol, contrary to the finding of Toyama (*Chem. Umschau*, 1924, **31**, 61), does actually exhibit small but definite optical activity, its specific rotation in chloroform being $[\alpha]_{5461}^{20^\circ}$ $+2{\cdot}6^\circ$ (*c*, 0·95). The activity is more readily demonstrated with batyl acetate, the specific rotation of which is $[\alpha]_{5461}^{20^\circ} - 8{\cdot}5^\circ$ in chloroform (*c*, 2·63).

The batyl alcohol used in these experiments was prepared by the direct hydrogenation of the unsaponifiable fraction (mainly selachyl alcohol) of the liver oil of *Centrophorus granulosus*. It thus follows that selachyl alcohol must be formulated as α-oleyl glyceryl ether, a conclusion in agreement with its recorded optical activity (Toyama, *loc. cit.*).

EXPERIMENTAL.

Batyl Alcohol.—The liver oil from *Centrophorus granulosus* freed from squalene (Heilbron and Owens, J., 1928, 942) was refluxed for 4 hr. with 150 g. KOH in 1250 c.c. EtOH and after removal of half the EtOH under reduced press. the residue was diluted with H_2O and thoroughly extracted with Et_2O. The combined extracts were washed with H_2O until free from soap, and dried over anhyd. Na_2SO_4. The mobile orange oil after removal of solvent (25 g.) was dissolved in MeOH (150 c.c.), kept for 25 hr. at − 10°, and the filtered solution hydrogenated under 2 atm. press. by Skita's method (*Ber.*, 1912, **45**, 3312). The absorption of H was complete after 3 hr. (1740 c.c. Calc. for pure selachyl alcohol, 1640 c.c.). Towards the end of the reaction batyl alcohol began to separate and, after filtration of the warmed solution, was obtained in almost quant. yield, m. p. 63—65°. Pure batyl alcohol, m. p. 70—71° (from EtOH), was obtained by conversion into and regeneration from its diacetate, which after fractional distillation (b. p. 223—227°/4 mm.), followed by crystn. from EtOH, had m. p. 36—36·5° (Toyama, *loc. cit.*, gives m. p. 33·9—34·4°) (Found : C, 69·4; H, 11·2. Calc. for $C_{25}H_{48}O_5$: C, 70·0; H, 11·2%).

Oxidation of Batyl Alcohol with Lead Tetra-acetate.—Batyl alcohol (10 g.), dissolved in AcOH (30 c.c.) previously freed from aldehyde by refluxing it for 4 hr. with CrO_3, was shaken at room temp. for 20 hr. with *N*/10-lead tetra-acetate (Dimroth, *Ber.*, 1923, **56**, 1375) in AcOH (1000 c.c.). The bulk of the solvent was removed by distillation, the first 50 c.c. being collected separately. This portion was diluted with an equal vol. of H_2O and treated with a warm solution of 2 : 4-dinitrophenylhydrazine in AcOH. The yellow amorphous solid deposited on cooling, after repeated crystn. from aq. EtOH, was obtained in feathery orange-yellow needles; m. p. 162—163°, alone or mixed with formaldehyde-2 : 4-dinitrophenylhydrazone, m. p. 163°, prepared from formalin (Purgotti, *Gazzetta*, 1894, **24**, 564, gives m. p. 155°).

The residue was diluted with H_2O, and the pptd. aldehyde washed with NaOAc–KI aq., $Na_2S_2O_3$ aq., and H_2O. *Glycollaldehyde octadecyl ether*, which does not give a positive Schiff reaction but rapidly reduces Tollens' reagent, crystallises from EtOH as a colourless solid, m. p. 51° (Found : C, 77·0; H, 12·9. $C_{20}H_{40}O_2$ requires C, 76·9; H, 12·8%). The 2 : *4-dinitrophenylhydrazone* obtained by Allen's method (*J. Amer. Chem. Soc.*, 1930, **52**, 2955) separates from EtOH in yellow needles, m. p. 73° (Found : C, 63·8; H, 9·1. $C_{26}H_{44}O_5N_4$ requires C, 63·4; H, 9·0%).

Glycollaldehyde octadecyl ether was also prepared in poor yield by passing a stream of ozonised oxygen through a solution of octadecyl allyl ether (Davies, Heilbron, and Owens, *loc. cit.*) in aldehyde-free AcOH for 3½ hr. After steam distillation until the distillate showed a negative Schiff reaction, the non-volatile residue was extracted with Et_2O, the extract washed (Na_2CO_3 aq.) and dried, and the aldehyde recovered and crystallised from EtOH; m. p. 51°, alone or mixed with the aldehyde obtained from batyl alcohol (Found : C, 77·2; H, 12·8%).

Glycollic Acid Octadecyl Ether.—A solution of glycollaldehyde octadecyl ether (6 g.) in warm AcOH (30 c.c.) was slowly treated with a solution of CrO_3 (1 g.) in AcOH (30 c.c.)–H_2O (10 c.c.). The whole was maintained at 70—80° for ½ hr., poured into H_2O, and extracted with Et_2O.

Addition of Na_2CO_3 aq. to the washed extract pptd. the sparingly sol. Na salt of the acid, which was repeatedly washed with Et_2O. The free acid crystallised from EtOH or light petroleum in small needles, m. p. 62—63° (Found : C, 73·5; H, 12·0. $C_{20}H_{40}O_3$ requires C, 73·2; H, 12·2%). *Ethyl glycollate octadecyl ether* was prepared (4 g.) by refluxing the acid (4 g.) in abs. EtOH (30 g.) containing 5% by wt. of conc. H_2SO_4 for 6 hr. The reaction mixture was poured into H_2O, and the *ester* extracted with Et_2O, washed, and dried. After removal of solvent the residue was repeatedly crystallised from EtOH, from which it separated as a wax, m. p. 41—42° (Found : C, 74·5; H, 12·8. $C_{22}H_{44}O_3$ requires C, 74·2; H, 12·5%). Treatment of the ester with alc. NH_2Me for 3 days at room temp. yielded the *methylamide*, $C_{18}H_{37}{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NHMe$, which crystallised from EtOH in short needles, m. p. 83—84° (Found : N, 3·8. $C_{21}H_{43}O_2N$ requires N, 4·1%).

α-Octadecyl Glyceryl Ether.—This was prepared by a modification of Davies, Heilbron, and Owens' method (*loc. cit.*) in order to compare the m. p.'s of the product and that obtained by those authors. A cold solution of perbenzoic acid in $CHCl_3$ (290 c.c. containing 8·6 g. perbenzoic acid) was added to a solution of octadecyl allyl ether (16 g.) in $CHCl_3$, and the mixture maintained at room temp. for 96 hr. Removal of solvent, after washing with Na_2CO_3 aq., left a low-melting solid, which was refluxed for 6 hr. with EtOH (300 c.c.) containing $2N$-H_2SO_4 (100 c.c.). Crude α-octadecyl glyceryl ether separated on cooling and was repeatedly crystallised from EtOH; m. p. 70—71° (yield, 10 g.). This ether was identical with that previously described, but admixed with natural batyl alcohol still showed a depression of fully 2° in m. p.

We desire to express our thanks to Dr. A. R. Todd of Oxford University for kindly carrying out the polarimetric determinations.

UNIVERSITY OF LIVERPOOL [*Received, December* 21*st*, 1932.]