LETTERS TO THE EDITORS

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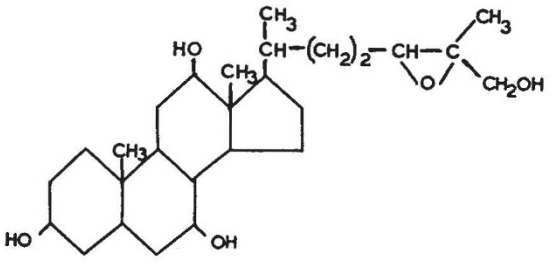
IN THE PRESENT CIRCUMSTANCES, PROOFS OF "LETTERS" WILL NOT BE SUBMITTED TO CORRESPONDENTS OUTSIDE GREAT BRITAIN.

Bile Acids of Elasmobranch Fish

THE bile of bony fishes, like that of birds and mammals, contains acids in which glycine or taurine is conjugated with mono-, di-, and tri-hydroxy derivatives of cholanic acid. On the other hand, Hammarsten[1] isolated from the bile of the shark, *Scymnus borealis*, acids which he showed to be sulphuric esters of neutral compounds, chiefly α-scymnol. The constitution of scymnol has been largely elucidated by the investigations of Windaus, Bergmann and König[2], and of Tschesche[3], who have shown that the compound is related to the commoner bile acids, but contains eight carbon atoms in the side chain like cholesterol, whereas the usual bile acids contain only five. This has considerable bearing on the view that the bile acids arise from the degradation of cholesterol, and it has been suggested[2] that the shark, which belongs to a primitive order of fish, lacks the ability to effect more extensive oxidation of cholesterol to the bile acids. This is evidently not entirely true, for Ota[4] has recently isolated cholic acid as well as scymnol from the bile of a species of shark found in Japanese waters.

The correspondence in positions and configurations of the nuclear hydroxyl groups of scymnol and cholic acid has been established by Ashikari[5] who degraded scymnol to cholic acid. The following is accordingly the structure of scymnol, the evidence for the ethylene oxide ring being somewhat inconclusive.



The scymnol used by Ashikari was isolated from the bile of *Dasyatis akajei*, a species of sting ray found in Japanese waters. An examination has now been made of the bile of the blue skate, *Raia batis*, and the grey dogfish, *Squalus acanthias*, caught off the Faroes during the summer and autumn. Immediately after the fish were killed the gall bladders were squeezed into a large excess of absolute alcohol, and the alcoholic bile was afterwards worked up as described by Windaus *et al.*[2] Pure scymnol, m.p. 192–193° (corr.) was readily isolated in considerable quantity, from the bile of both of these cartilaginous fish. It had $[\alpha]_D^{15°} = +39{\cdot}4°$ ($c = 2{\cdot}614$ in alcohol, (found: C, 72·1; H, 10·1. calc. for $C_{27}H_{46}O_5$, C, 71·9; H, 10·3 per cent). There were minor amounts of resinous bile acids from which a pure component has not yet been isolated. Alkaline hydrolysis of the bile from the teleostean angler fish (*Lophius piscatorius*) gave no water-insoluble product so that scymnol-sulphuric acid was not present. Scymnol, esterified with sulphuric acid, thus appears to be a characteristic major component of the bile of elasmobranch fish.

The scymnol obtained from the skate bile was further characterized by conversion into the dihydrate[6], the hydrochloride[2], and the tetra-acetyl derivative[3] (this was prepared by Dr. J. D. Loudon). In preliminary experiments on the isolation from both skate bile and dogfish bile complications arose from the fact that purification of the crude dihydrate by crystallization from ethyl acetate gave a product which formed colourless slender needles, m.p. 138–140°. This evidently still contained water of crystallization. (Found: C, 70·7; H, 10·4. $C_{27}H_{46}O_5, \frac{1}{2}H_2O$ requires C, 70·5; 10·3 per cent.) Its formation was apparently associated with the quality of the ethyl acetate, for it was rapidly and completely transformed into anhydrous scymnol when warmed with pure ethyl acetate obtained from another source.

This investigation, which is being continued, was made possible by the co-operation of Dr. J. A. Lovern, of the Torry Research Station, Aberdeen (Department of Scientific and Industrial Research) who kindly arranged for the collection of the bile.

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Feb. 22.

[1] Hammarsten, O., *Z. physiol. Chem.*, **24**, 322 (1898).
[2] Windaus, A., Bergmann, W., and König, G., *Z. physiol. Chem.*, **189**, 148 (1930).
[3] Tschesche, R., *Z. physiol. Chem.*, **203**, 263 (1931).
[4] Ota, K., *J. Biochem.* (Japan), **29**, 241 (1939).
[5] Ashikari, H., *J. Biochem.* (Japan), p. 319.
[6] Compare Oikawa, S., *J. Biochem.* (Japan), **5**, 63 (1925).

Insect Cuticle as an Asymmetrical Membrane

IN a recent communication[1], I provided evidence to show that the permeability of the outer 'lipoid layer' of insect cuticle to feebly dissociating substances of high dielectric constant may be greatly increased by relatively apolar substances of low dielectric constant. Since then I have obtained similar results for the outer cutinized layers of a number of plant epidermal membranes. The physical and chemical properties of plant 'cutin' are said to resemble those of the insect 'epicuticle' or 'lipoid layer'[2], and this suggested that induced penetration of polar substances was not a fundamental characteristic of insect cuticle, but might take place with relatively simpler artificial membranes.