XXXII. SURFACE FILMS OF BATYL, CHIMYL AND SELACHYL ALCOHOLS.

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THE isolation of quantities of batyl, chimyl and selachyl alcohols by Drummond and Baker [1929] in this laboratory provided an opportunity to examine thin films of a type of molecule not hitherto studied. Batyl alcohol has been shown by Heilbron and Owens [1928] to be an ether of octadecyl alcohol and glycerol. Selachyl alcohol is the corresponding glyceryl ether of oleyl alcohol, and chimyl alcohol the cetyl alcohol derivative [Drummond and Baker, 1929].

The three compounds have therefore the same type of structure, namely a long hydrocarbon chain attached by an oxygen atom to a glycerol group at either the α - or β -carbon atom:

where $n = 18$ for batyl alcohol or 16 for chimyl alcohol.

In selachyl alcohol the hydrocarbon chain is probably

but the position of the double bond is not definitely known.

Heilbron and Owens [1928] gave reasons for believing that the β -structure was the correct one. More recently, however [Heilbron, 1929], it is stated that attempts are being made to synthesise structures of the α -type, this being regarded as the more probable structure. The measurements on the films to be described in this paper provide strong evidence in favour of the α -structure.

EXPERIMENTAL.

The apparatus and technique used in the study of monomolecular films have been fully described by Adam and Jessop [1926]. Dilute solutions of the several alcohols in benzene were accurately prepared. The benzene was re-fractionated and finally distilled in an all-glass (pyrex) apparatus before use. It left no residual film upon water. A small quantity of solution was placed upon a clean water surface in a Langmuir-Adam trough by means of a capillary drop-pipette.

The water used in the trough was laboratory-distilled, further purified by redistillation from alkaline permanganate in a large pyrex still with ground joints. Before a film was applied the water surface was always tested for contamination by sliding the barrier to within 2 cm. of the float of the torsion apparatus. No deflexion is noted if the surface is clean.

Materials. One sample of batyl alcohol had been obtained from the liver oil of the Greenland shark, *Somniosus microcephalus*. It had been purified by several recrystallisations from ether and melted at 69°. Another specimen had been obtained by the hydrogenation of selachyl alcohol. After purification it also melted at 69°. The specimen of chimyl alcohol was isolated from Japanese shark-liver oil and after recrystallisation from ether melted at 62–62.5°.

The selachyl alcohol was fractionated from Japanese shark-liver oil and purified by refractionation. It boiled at 236–239° at 5 mm., but the iodine value was slightly higher than the theoretical.

The films of the three alcohols were studied between 0° and 40°, a range which includes the transition temperatures from condensed to expanded films of batyl and chimyl alcohols.

DISCUSSION.

The results of the measurements are illustrated by the curves in Figs. 1 and 2, which show the relation between the area occupied by one molecule in the film and the compressing force.

Fig. 1.

The films of batyl alcohol and chimyl alcohol showed a close resemblance to those of the α -monoglycerides [Adam, Berry and Turner, 1928], both condensed and expanded films being formed. The curves for chimyl alcohol are

identical with those of α -monopalmitin at every temperature, within experimental error: the condensed and expanded films, the transition region and the temperature of expansion being practically the same.

Fig. 2.

Condensed films. The condensed films are liquid, as shown by the movement of talc particles scattered on the surface. The films are of the close-packed head variety, with slight rearrangement under pressures greater than about 6 dynes/cm. The values for the cross-section of the molecule for the two arrangements (extrapolated graphically to zero pressure) are included in Table I.

Table I.

	Cross-section, sq. Å. per molecule		
	Head	Rearranged	Difference
α -Monoglycerides	26.3	—	—
Batyl alcohol	26.0	24.8	1.2
Chimyl alcohol	28.6	27.4	1.2
(Difference)	(2.6)	(2.6)	—
Mono-octadecylmalonic acid	36	—	—

All values ± 0.4 sq. Å.

It will be seen that the curves for the condensed films of the two substances are sensibly parallel, with chimyl alcohol about 2.6 units greater in area. This may be due to a slight trace of unsaturated impurity which might be expected from the mode of preparation. The values for the cross-section given by batyl alcohol are probably more nearly correct. They agree very closely with the values found by Adam, Berry and Turner for α -monoglycerides, namely 26.3 ± 0.5 sq. Å.

This agreement is interesting in that it suggests that batyl and chimyl alcohols are α -glyceryl ethers.

If batyl alcohol had the β structure I, since the two $-\text{CH}_2\text{OH}$ groups are symmetrically placed, it might be expected to orient itself at the water surface as in the figure. In this case it would be expected that the cross-section of the head would be considerably greater than the value for cetyl alcohol, which is 21.6 sq. Å., because two $-\text{CH}_2\text{OH}$ groups per molecule would have to be packed side by side. This is borne out by measurements of N. K. Adam (private communication) on mono-octadecylmalonic acid II. This gives a solid condensed film, with an area of about 36 sq. Å. at no compression.

If, on the other hand, batyl alcohol has the unsymmetrical α structure III, its orientation would be expected to be that of the α -monoglycerides IV, with "the three carbons of the glycerol nearly vertically above one another" [Adam, Berry and Turner, 1928]. The cross-sectional areas should therefore be the same.

The close agreement found experimentally is strong evidence in favour of the unsymmetrical α -structure for batyl and chimyl alcohols.

Expanded films. On raising the temperature the liquid condensed films give liquid expanded films. The temperatures of half expansion at 2 dynes/cm. pressure are:

chimyl alcohol	17.5°
batyl alcohol	35.5°.

The expansion is of the usual type, with the transition region not horizontal.

In the expanded films the areas at no compression are:

chimyl alcohol	65.0 $\pm$ 3 sq. Å.
batyl alcohol	60.0 $\pm$ 3 sq. Å.
α -monoglycerides	70.0 $\pm$ 3 sq. Å.

These values are interesting as further examples of expanded films having an area at no compression differing considerably from the value 48 sq. Å. found for so many substances, and upon which had been based the coiled-chain hypothesis of the structure of these liquid expanded films. This hypothesis was abandoned when it was shown that *p*-dodecyl- and *p*-nonyl-phenols and

the α -monoglycerides gave areas differing from this value [Adam, Berry and Turner, 1928].

Selachyl alcohol also gives an expanded film but it is so much above its transition temperature that lowering the temperature to 0° does not cause it to condense.

SUMMARY.

Measurements have been made of monomolecular films of batyl, chimyl and selachyl alcohols between 0° and 40°.

The values for the cross-section of the heads of batyl and chimyl alcohols are compared with the value for α -monoglycerides. Evidence is adduced that these two alcohols have the unsymmetrical α -glyceryl ether structure.

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