LIII. SURFACE FILMS OF VITAMIN E CONCENTRATES.

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CERTAIN preparations described in the preceding paper [Drummond *et al.*, 1935] were examined by the method of surface films, with the object of obtaining information about their molecular structure. The substances examined included an oil concentrate rich in vitamin E, and the crystalline substance M.P. 190° (from acetate M.P. 236°, from E-active fractions 3 and 4).

The substances were spread on the surface of *N*/50 HCl and the surface pressures were measured by the method of Adam and Jessop [1926; Adam, 1930] and the surface potentials by the method of Adam and Harding [1933].

Vitamin E-active oil.

This substance, spread from benzene solution, gave the curve shown in Fig. 1, in which surface pressures are plotted as ordinates and values of area/molecule in sq. Å. as abscissae. The latter were calculated on the assumption

Fig. 1.

that the solute spread consisted of a substance with mol. wt.=390. Fig. 1 also shows the relation between surface potentials and area, and values of μ calculated from the equation

$$\delta V = 4\pi n\mu,$$

n being the number of molecules per sq. cm. μ measures the effective vertical component of the dipole moment of the molecule at the corresponding compression.

The surface pressure-area curves are consistent with the view that the substance is polycyclic, with a water-attracting group at or near one end of the molecule. The relatively high compressibility of the film and the limiting area of 63 sq. Å. are similar to those of ketones of the sterol series (*cf.* cholesterolone [Rosenheim and Adam, 1929]). If more than one polar group is present in the molecule, it is unlikely that they are far apart in the molecule. If this were so, one would expect the molecule to lie flat on the surface and give a film of the gaseous type (*cf.* pregnandiol, pregnandione, oestrone derivatives [Danielli *et al.*, 1933]).

The films of this substance collapsed when the surface pressure was greater than about 15 dynes/cm.; this collapse was reversible and examination of the films under the ultra-microscope by the method of Zocher and Stiebel [1930] showed the appearance of numbers of fine droplets at about this pressure. The films were unusual in that the reversible collapse was accompanied by a rise in surface pressure; this might be due to the presence of a less readily collapsing impurity. The possibility that the upper flattened portion of the curve was due to a transition between liquid expanded and condensed states was further excluded by measuring the surface pressure at a low temperature (1.5°), which resulted in a curve similar to the one obtained at room temperature (15°).

The moderate changes of surface potential and μ over the unimolecular portion of the film (below 15 dynes/cm.) indicate that only small alterations in the tilt of the molecule and the adhesion of the polar groups to the water took place on compression; beyond this point, where collapse occurred, μ appeared to fall more rapidly, but this was probably due to the area assumed in calculating μ being too small, owing to collapse.

Crystalline substance; M.P. 190°.

This substance on the surface of *N*/50 HCl gave the rather compressible solid film shown in Fig. 2, curve I. Extrapolation to zero pressure gave a limiting area of 47.6 sq. Å. On first compression the film contracted, but above 3 dynes/cm. pressure it formed a stable solid film. The values of surface potential and μ are also shown in Fig. 2.

The data suggest a polycyclic structure with the water-attracting group near one end of the molecule. The limiting area is much in excess of that required for long-chain compounds or terminal groups such as phenol or hexahydrophenol; on the other hand reduced polycyclic structures such as sterols give curves showing limiting areas ranging from 38 sq. Å. upwards, according to the position of the water-attracting group. Among compounds of this type, cholesterol-6-ol shows an area of 48 sq. Å. and its surface pressure curve is similar to that of the crystalline substance obtained from vitamin E preparations. The surface potential is somewhat lower.

The empirical formula ($C_{30}H_{50}O$) for the crystalline substance is the same as that of the amyirin series of compounds. These substances are known to be polycyclic, probably containing five rings, and have a hydroxyl group in a position not yet definitely ascertained [Ruzicka *et al.*, 1929; Spring, 1933]. As has been shown in the preceding paper [Drummond *et al.*, 1935] the melting-points of the crystalline vitamin E derivative and its acetate closely correspond with those of β -amyirin. Accordingly, the surface properties of a specimen of β -amyirin were investigated. The results are shown in Fig. 2. On first compression the film showed marked contraction; this effect was similar to that observed with the crystalline substance itself, but occurred to a much greater

extent. The initial course which the curve tended to follow is shown as curve III A in Fig. 2. The film rapidly rearranged to give a stable solid film (curve III), rising fairly steeply and tending to a limiting area at zero compression of 47 sq. Å. This initial contraction and rearrangement to give a solid film is common to several substances of the amyirin group (Askew; unpublished measurements).

Fig. 2. I. Crystalline substance. II. Cholestane-6-ol. III. β -Amyrin (contracted film). III A. β -Amyrin (initial film). IV. Combined curve, 80 % β -amyirin, 20 % vit. E oil.

The surface pressures of the two substances, although they approach approximately the same limiting areas, differ in two respects: (a) that of β -amyirin is much steeper, (b) it shows the rearrangement phenomena to a much more marked extent. In view of the similarity of the other properties of these two substances and the similarity of their limiting areas, experiments were performed to see whether these differences could be accounted for by impurities in the specimen of the crystalline substance. A mixture of 80 molecules % of β -amyirin and 20 molecules % of the vitamin E-rich oil was spread on the same surface. The resulting curve is shown as curve IV, Fig. 2. The tendency to form a contracting film was greatly diminished, and the slope of the curve approximated to that of the crystalline substance. Hence it appears that the properties of these substances may be greatly modified by the presence of impurities, and a more complete check on the identity of the crystalline substance with β -amyirin awaits the preparation of larger quantities of purified material. At present it can be stated that the substance almost certainly has a polycyclic structure, akin to that of the sterols, with a polar group, most probably a hydroxyl group, near one end of the molecule; that it closely resembles in some of its surface properties substances of the amyirin type, and that the surface data are consistent with the view that the substance is β -amyirin. The surface potentials of the crystalline substance and β -amyirin were of the same order of magnitude, but that of the latter appeared to rise more steeply; this is however uncertain, owing to the tendency of the film to rearrange in the initial stages of compression. The rearrangement was not accompanied by large changes in surface potential.

SUMMARY.

A concentrate rich in vitamin E and a crystalline substance derived from vitamin E preparations have been examined by the method of surface films.

Both substances appear to have condensed polycyclic structures.

The possibility that the crystalline substance is identical with β -amyrin is discussed in the light of surface film data.

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