

to the publication. Further, I thank Professor A. Tovborg Jensen for some grams of potassium perrhenate, and Miss Bodil Friis for assistance with the preparations.

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Mixed Monolayers of Isodextropimaric and Normal Long Chain Fatty Acids

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In a previous study¹ it was found that the average area per molecule in fatty acid monolayers containing different amounts of isodextropimaric acid (IdP) was higher than that expected if the mixtures behaved ideally. The work described in this paper, which is a continuation of the earlier investigation, has yielded data for mixed monolayers with high ratios of IdP to fatty acids. The data will be compared with theoretical deductions based on an assumed structure for the mixed monolayers.

The variation of the average area per molecule measured at a surface pressure of 1.5 dynes per cm with the composition of the IdP-fatty acid monolayers is shown in Fig. 1. The experimental details have

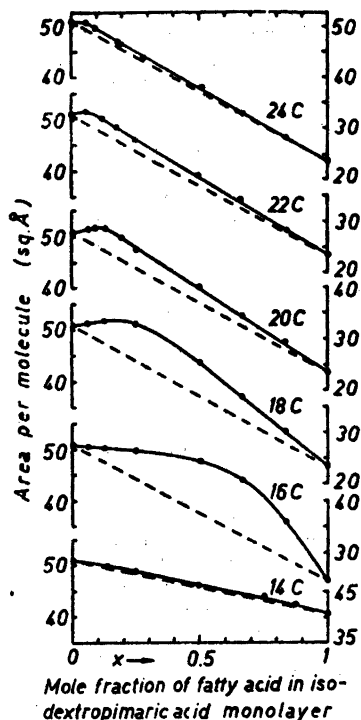


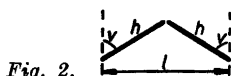
Fig. 1. Molecular areas of isodextropimaric acid monolayers containing normal fatty acids (C_{14} — C_{24}). Surface pressure, 1.5 dynes/cm. Substrate: dilute HCl (pH 3). 20° C.

been described in the earlier paper¹. Except for the mixtures containing myristic acid (Curve C 14), which are of the expanded type at room temperatures, positive deviations from the ideal behaviour ($A_{\text{mixt.}} = x_1 A_1 + x_2 A_2$, the dotted lines) are evident in the curves. The expansions are greatest for the layers containing palmitic acid (Curve C 16) and decrease as the chain length of the fatty acid increases. At the same time, the maximal expansion shifts to lower fatty acid contents.

Owing to the different dimensions of the molecules of the components, the hydrocarbon part of the mixed monolayer may be considered as being composed of two layers, an upper layer formed by the parts of the flexible fatty acid chains that project above the IdP-molecules and a lower densely packed layer comprising bulky inflexible IdP-molecules and the lower parts of the

fatty acid chains. It is obvious that the average area per molecule in this "double" layer is primarily determined by the conditions prevailing in the densely packed lower layer, but it may be assumed to be mechanically influenced by the thermal agitation of the free chains in the upper layer. This latter expanding effect may be expected to increase with increasing fatty acid content when the latter is low since the projecting chains will not then affect each other's agitation owing to the large distances between them. At higher fatty acid contents, when the molecules are closely situated in the upper layer, the chains will interact and hence the agitation of the fatty acid chains will be more or less restricted. Owing to this the expansion of the layer will decrease with increasing fatty acid content. In view of the fact that the intermolecular forces between the hydrocarbon chains have a very short range, it seems probable that the maximum expansion occurs at the fatty acid content at which the agitating upper ends of the molecules first come into contact.

If the parts of the hydrocarbon chains in the upper layer are considered as swinging rods of small diameter (Fig. 2), the distance



l between the axes of deflection of the two rods, the upper ends of which touch each other, is related to the length h of the rods by the equation

$$l = \sin v \times 2 h \quad (1)$$

where v is the angle of deflection from the vertical. If the angle v is independent of h , we may write

$$dl/dh = \sin v \times 2 \quad (2)$$

The mean distance l_m between the centres of two closest fatty acid molecules at maximum expansion of the monolayer can be calculated from the equation

$$l_m = \frac{4\sqrt{108}}{3} \cdot \left(\frac{1-x}{x} \cdot \bar{A}_{\text{IdP}} + \bar{A}_{\text{F}} \right)^{\frac{1}{2}} \quad (3)$$

in which x denotes the mole fraction of fatty acid and \bar{A}_{F} and \bar{A}_{IdP} the respective partial molecular areas of the fatty acid and IdP. Values of l_m based on the experimental data are given in Table 1.

Table 1.

Number of C-atoms in fatty acid	x (at maximal expansion)	\bar{A}_{IdP} (\AA^2)	\bar{A}_{F} (\AA^2)	l_m from Eq. (3)	h_{F} from Eq. (4)
16	0.60	59.5	37.0	9.4	8.4
18	0.32	58.0	31.5	13.4	11.0
20	0.17	56.0	24.0	18.5	13.5
22	0.10	53.5	23.5	24.1	16.0
24	0.07	52.5	23.5	28.9	18.6

The maximal length of a fatty acid molecule is found on the basis of bond lengths and atomic radii to be $(1.27 \times n_c + 4.0) \text{\AA}$ where n_c denotes the number of carbon atoms in the molecule. The length of the IdP-molecule² is 15.8\AA . The length of the part of the fatty acid molecule projecting above the IdP-molecules is hence

$$h_{\text{F}} = (1.27 \times n_c - 11.9) \text{\AA} \quad (4)$$

When l_m is plotted against h_{F} for the different fatty acid-IdP-layers, the following linear equation is obtained:

$$l_m = 2 h_{\text{F}} - 8 \text{\AA} \quad (5)$$

The slope of this line is 2, in agreement with Eq. (2) when $\sin v = 1$, *i. e.* when the angle of deflection is 90° . (Calculations based on data recorded at a surface pressure of 10 dynes per cm give the same slope.)

By substituting $l_m = 0$ in Eq. (5), the value $h_{\text{F}} = 4 \text{\AA}$ is found which gives the length of the ineffective part of the chain forming the upper layer that does not contribute to the sideward deflection of the chain. This length probably corresponds to the curved part of the deflected hydrocarbon chain.

It seems that a method based on this theory of folding of fatty acid molecules around other molecules can be developed which will permit a relatively accurate determination of the dimensions of molecules in mixed monolayers. \square

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Sialic Acid in Pseudomyxomatous Gels

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It is well known that glycoproteins occur in considerable amounts in the contents of certain types of ovarian cysts. Little recent work, however, has been published on the nature of these glycoproteins, except for the extensively studied blood-group substances, which were shown to occur in pseudomucinous cyst fluids by Morgan and van Heyningen¹. The carbohydrate component of the blood-group substances has been shown to consist of glucosamine, galactosamine, galactose, and fucose²⁻⁴. Hiyama⁵ has isolated the hexosamines and galactose from the gelatinous 'paramucin' of an ovarian cyst, noting that the material gave the 'direct Ehrlich' reaction, *i. e.* it gave a violet colour when heated with Ehrlich's *p*-dimethylaminobenzaldehyde reagent without previous treatment with alkali. Jensen⁶ has isolated a product from a few pseudomucinous cyst fluids thought to be hyaluronic acid. (I have not been able to find this substance in the same type of cysts.)

In a study on the protein and glycoprotein components of a great number of ovarian cyst contents and their relation to the histological type of the cysts, I have found that pseudomyxomatous gels differ not only physically but also chemically from ordinary pseudomucin. An obvious difference is the much higher content of

sialic acid in the gels (about 10 % compared with 1-2 %, as determined colorimetrically). Sialic acid has now been isolated in crystalline form from this material, and by chemical analysis and X-ray powder diagrams is shown to be identical with the sialic acid prepared by Blix *et al.*⁷ from the submaxillary mucin of sheep.

The pseudomyxomatous material, which forms a water-insoluble gel, was washed with water and broken up in a Turmix blender. After several days in ethanol, when the gel had shrunk considerably, it was ground in a mortar and after further treatment with ethanol and ether, dried in a desiccator.

The results of analysis of a typical preparation from a cyst-gel are given in Table 1.

Table 1.

Nitrogen (Micro-Kjeldahl)	10.2 %
Glucosamine-HCl *	5.8 %
Galactosamine-HCl *	5.7 %
Galactose **	3.6 %
Mannose **	0.6 %
Fucose **	2.1 %
Sialic acid ***	11.8 %
Ester-sulphate	0.1 %
Ash	3.7 %

* Chromatographic separation of the hexosamines by Gardell's method⁸.

** Vasseur's modification of the Tillmanns-Philippi orcinol reaction⁹ and a quantitative paper chromatographic method.

*** Colour reactions with Bial's and Ehrlich's reagents¹⁰.

From this material, thoroughly freed from inorganic matter by treatment with very dilute hydrochloric acid, sialic acid was prepared according to the principles set out by Blix¹¹.

10 g of the dry powder was suspended in 200 ml of water, and heated for one hour on a boiling water-bath. The suspension was centrifuged, and the supernatant filtered and freeze-dried. The small amount of material obtained was extracted with methanol, and the solvent



Fig. 1. X-ray powder diagram of sialic acid from an ovarian cyst-gel.