

for $C_{18}H_{24}O_6$: C 56.1; H 6.59; OCH, 14.5.) Acetylation of the crystalline racemate or of the anhydrous product yielded a tetraacetate of m. p. 86–88°, identical with the previously⁹ described acetate (VIII) of m. p. 84–85°, which obviously was not quite pure. Acetylation of the non-crystallizable residue obtained from the mother-liquors of the crystalline guaiacylglycerol furnished the second tetraacetate (VIII), m. p. 113–114°.

We further want to report the synthesis of the phenolic guaiacylglycerol- β -guaiacyl ether (III). It was carried out in a manner analogous to the preparation of the corresponding methyl ether (II). The reaction of ω -bromo-benzoyl-acetoguaiacone¹ with guaiacol in anhydrous methyl ethyl ketone in the presence of anhydrous potassium carbonate gave ω -(2-methoxy-phenoxy)-benzoyl-acetoguaiacone, which was treated in abs. ethanol with paraformaldehyde and potassium carbonate at room temperature. Reduction of the resulting α -(2-methoxy-phenoxy)- β -hydroxy-propioguaiacone with lithium aluminium hydride yielded the crude substance III as a syrup, from which a crystalline triacetate (IV), m. p. 106–108°, was obtained. (Found: C 62.0; H 6.08; OCH, 14.06; CH_2CO 28.5. Calc. for $C_{28}H_{36}O_9$: C 61.8; H 5.86; OCH, 13.90; CH_2CO 28.9.) The acetyl groups were removed from this triacetate by reduction with $LiAlH_4$. The guaiacylglycerol- β -guaiacyl ether (III) thus obtained was a practically colourless syrup. On re-acetylation the triacetate IV was again obtained.

Very recently, Freudenberg¹⁰ has synthesized substance V by a similar procedure and has shown that one of the three dimeric products previously obtained on enzymatic dehydrogenation of coniferyl alcohol¹¹ is identical with this substance.

The view expressed by Adler and Lindgren²⁻⁵ that guaiacylglycerol- β -aryl ether structures (I) may be essential elements in lignin has thus received further substantial support.

Details regarding the synthesis of III and of related compounds as well as their behaviour in typical lignin reactions, especially in ethanolysis, will be published later.

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Expansion of Condensed Monolayers of Normal Long Chain Fatty Acids on Admixture of Isodextropimaric Acid

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Previous investigations^{1,2} have shown that myristic and other long chain fatty acids, which give expanded monolayers in pure form, yield condensed monolayers when cholesterol and certain other bulky molecules are added to them. In the following an admixture-effect will be described which is the opposite of the above, *i. e.* an expansion of condensed fatty acid monolayers occurs on addition of a foreign substance, which alone forms a monolayer of the condensed type.

The study was conducted with a continuously recording surface balance of the Wilhelmy-Dervichian type³. The fatty acids investigated were palmitic, stearic, arachidic, behenic, lignoceric and myristic acids, of which the last-mentioned forms a monolayer of the expanded type. As the admixture-substance, isodextropimaric acid⁴, a rosin acid, was employed.

* For a detailed investigation of the monolayer properties of this and other rosin acids, see references 4 and 5.

In Fig. 1 are plotted the areas per molecule of monolayers containing different contents of isodextropimaric acid (IdP); these relate to a surface pressure of 1.5 dynes/cm*. The palmitic-IdP layers (Curve 16 C) are seen to exhibit much higher area values than would be expected if the monolayer behaved as an ideal mixture, *i. e.* if the molecular area of the mixture were given by the expression $A_{\text{mixt.}} = x_1 A_1 + x_2 A_2$ (dotted line). The area increase is also considerable for the stearic-IdP layers (Curve 18 C), but only relatively slight for the arachidic-IdP layers (Curve 20 C), and very small for the behenic-IdP layers (curve 22 C). The areas for the lignoceric-IdP layers follow the ideal curve,

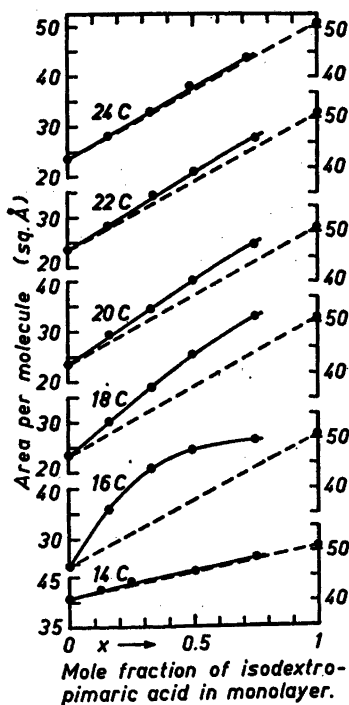


Fig. 1. Molecular areas of normal fatty acid monolayers (C_{14} — C_{24}) containing isodextropimaric acid. Surface pressure, 1.5 dynes/cm. Dotted lines: calculated molecular areas corresponding to ideal behaviour. Substrate: dilute HCl (pH 3). 20° C.

* This pressure is frequently employed when defining areas of monolayers of aliphatic long chain compounds.

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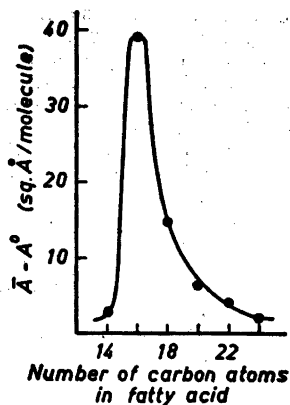


Fig. 2. Expansion of fatty acid monolayers containing isodextropimaric acid (mole fraction $x = 0.1$). Ordinate: difference between partial molecular area for isodextropimaric acid in the fatty acid monolayer and the molecular area in the pure isodextropimaric acid monolayer. Surface pressure, 1.5 dynes/cm. Substrate: dilute HCl (pH 3). 20° C.

as also do those for the myristic-IdP layers (Curve 14 C). In Fig. 2 the difference between the actual partial molecular area \bar{A} as determined by the tangent method and the molecular area A° for the pure substance is plotted for isodextropimaric acid (mole fraction $x = 0.1$) against the number of carbon atoms of the fatty acid forming the other component of the mixture. The different degrees of expansion become clearly evident from the diagram.

Palmitic acid is the first fatty acid with increasing chain length that at room temperature forms a condensed monolayer. It possesses a hydrocarbon chain of sufficient length to give rise to a lateral attraction strong enough to overcome the thermal agitation of the flexible chains. When IdP molecules are added to its monolayer, they force apart the densely packed palmitic acid molecules and owing to their short length (IdP 16 Å, palmitic acid 24 Å) they are able to fill only the lower parts of the openings formed. The lateral attraction, composed of the attraction between the palmitic and IdP molecules and between the upper ends of the former molecules becomes insufficient to maintain a condensed monolayer. With increasing chain length however, the lateral attraction gradually

increases, until in the case of lignoceric acid, for which the part of the chain projecting above the IdP molecules has a length of about 19 Å, it is sufficient to effect complete condensation even in the presence of IdP molecules.

It may be noted that also in other systems formed by flexible long chain molecules and rosin acid molecules, the relative lengths of the molecules play an important part. In solutions of binary mixtures of rosin acid soap and fatty acid soaps, mixed micelle formation occurs when the fatty acid soaps are sodium myristate and laurate, but not in the case of sodium palmitate and oleate⁶.

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Self-diffusion and Viscosity in Liquids

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In this preliminary communication some problems connected with self-diffusion and viscosity in liquids are treated using a modified kinetic theory. The molecules of a liquid are assumed to move in jumps between equilibrium positions by passing across a potential barrier, ΔF . For a pure liquid in thermodynamic equilibrium, the

mole flow from left to right through a unit area normal to the x -direction, is given by

$$\text{Flow}_{x \rightarrow} = v \cdot c / 6 \quad (1)$$

where c is the concentration in moles/cm³. The velocity of the molecules v is equal to $p \cdot \lambda$, where λ is the mean distance between successive equilibrium positions and p is the number of jumps per sec for which an exponential expression should be used. The mole flow may then be written

$$\text{Flow}_{x \rightarrow} = D \cdot c / \lambda \quad (2)$$

where $D = p\lambda^2/6$ is the coefficient of self-diffusion. In equilibrium the same flow takes place in the opposite direction and the net flow is zero.

If there is a concentration gradient and D is independent of $c(x)$, the net rate of flow becomes

$$\text{net Flow} = \frac{\partial}{\partial c} \text{Flow}_{x \rightarrow} \cdot \Delta c = D \cdot \frac{dc}{dx} \quad (3)$$

since $\Delta c = \lambda \cdot dc/dx$, and Ficks law is obtained.

The diffusion of a group of n arbitrary molecules in the liquid is then considered. The vectorial displacement of the group centroid, when each molecule in the group has made an independent jump, is given by

$$\bar{\lambda}_n = \frac{1}{n} \sum_1^n \bar{\lambda} \quad (4)$$

The average numerical value of $\bar{\lambda}_n$ for a large group, or a large number of small groups, is

$$\lambda_n = \frac{1}{\sqrt{n}} \cdot \lambda \quad (5)$$

The flow of such groups in equilibrium (cf. eqs. (1) and (2)) is then

$$\text{Flow}_{x \rightarrow} = D_n \cdot c_n / \lambda \quad \text{with } D_n = \frac{p \cdot \lambda^2}{6 \cdot \sqrt{n}} \quad (6, 7)$$

The activation energy of a solute molecule (or ion) in water, is supposed to be due to the formation of hydrogen bonds between this and the water molecules, the solute molecule being able to establish a certain maximum number n_s of hydrogen bonds according to its molecular structure. Only a fraction of these hydrogen bonds are established at any time, and this fraction is continually changing. It is postulated that the diffusion coefficient of the solute molecule is equal to the diffusion coefficient of the surrounding group of n_s water molecules. If Eyring's expression for p is used, the diffusion coefficient becomes