

**Monolayers of Diastereoisomeric Long Chain Compounds.
The Behaviour of (+)-2(L),9(L)-Dimethyltetracosanoic
Acid, (+)-2(L),9(D)-Dimethyltetracosanoic Acid,
and the Corresponding 7-Keto Acids**

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Diastereoisomeric compounds usually exhibit large differences in the physical properties of their solid states. In the liquid state differences with regard to boiling point, refractive index etc. also exist, but in case of higher aliphatic compounds the differences in the liquid state are usually very small. It was of interest to study the properties of monolayers of diastereoisomeric long chain compounds in order to see whether differences in physical properties between diastereoisomers also exist in the two-dimensional states. The synthesis of the two dextrorotatory diastereoisomers of 2,9-dimethyltetracosanoic acid has recently been carried out¹ and the monolayer properties of these acids and the corresponding 7-keto acids will be described in the present communication.

That diastereoisomers may exhibit large differences in monolayer behaviour has been long known in case of sterols, for example the difference between cholestane-3-ol and *epi*-cholestane-3-ol², but no work appears previously to have been carried out with diastereoisomeric aliphatic compounds.

EXPERIMENTAL

Force-area curves were obtained of the acids spread on 0.01 *N* hydrochloric acid substrate and on a neutral substrate containing barium ions (BaCl_2 $0.3 \cdot 10^{-4}$ molar, KHCO_3 $4.0 \cdot 10^{-4}$ molar) with the aid of the recording mikrokator balance³. Spreading was effected from a solution in light petroleum (b. p. 60–80°) by means of the "Aglä" micro-syringe, the technique being the same as previously described⁴.

The results are shown in Figs. 1–8. The force-area curve for one of the diastereoisomers was first recorded, the barrier moved back again (the camera is mechanically

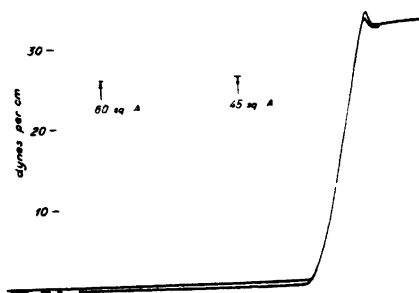


Fig. 1. Force-area curves for the two dextro-rotatory diastereoisomers of 2,9-dimethyltetracosanoic acid on 0.01 N HCl substrate at a temperature of 4.0°.

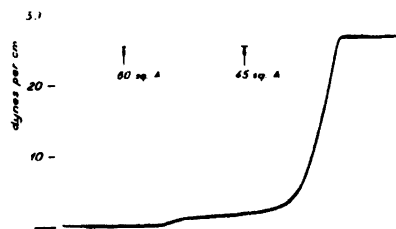


Fig. 2. Force-area curves for the two dextro-rotatory diastereoisomers of 2,9-dimethyltetracosanoic acid on 0.01 N HCl substrate at 13.5°.

linked to the barrier carriage) and the surface cleaned. The second diastereoisomer was then spread and its force-area curve recorded on the same paper as the first one. The Figs. 1–6 show that the force-area curves for the (+)-2(L), 9(D)- and (+)2-(L), 9(L)-dimethyltetracosanoic acids are identical both on acid substrate and on a neutral substrate containing barium ions. At low temperatures the monolayers are of the liquid condensed type. On HCl at 4° (Fig. 1) the limiting area is 38 sq. Å, and the monolayers collapse at a pressure of 32.5 dynes/cm and an area of 31 sq. Å. At higher temperatures (Figs. 2 and 3), the monolayers are of the liquid expanded type, and the force-area curves show a transition of the myristic acid type. On barium substrate the monolayers are more condensed than on acid substrate, the limiting area at a temperature of 5° (Fig. 4) being 34 sq. Å. In this case the stability of the films is also greater, and collapse takes place at 27.5 sq. Å and a pressure of 48 dynes/cm. At higher temperature the mono-

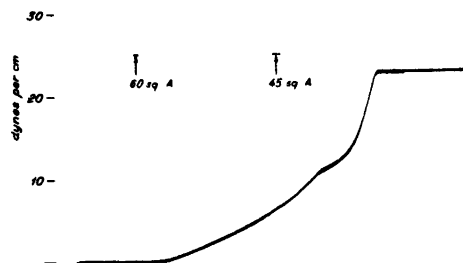


Fig. 3. Force-area curves for the two dextro-rotatory diastereoisomers of 2,9-dimethyltetracosanoic acid on 0.01 N HCl substrate at 20.0°.

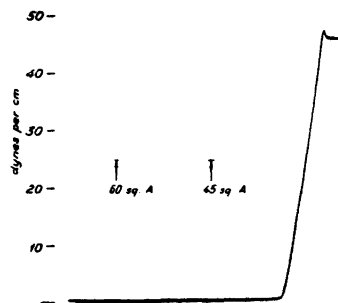


Fig. 4. Force-area curves for the two dextro-rotatory diastereoisomers of 2,9-dimethyltetracosanoic acid on barium substrate at 5°.

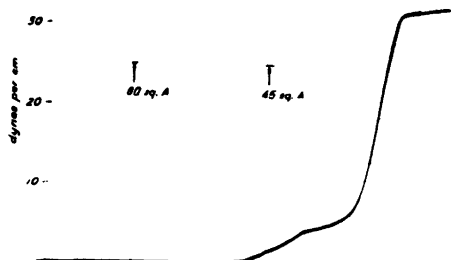


Fig. 5. Force-area curves for the two dextro-rotatory diastereoisomers of 2,9-dimethyltetracosanoic acid on barium substrate at 20.0°.

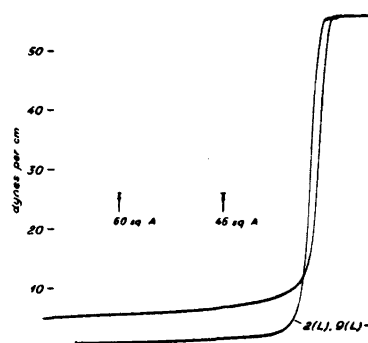


Fig. 6. Force-area curves for the stereoisomeric keto-acids on barium substrate at 5°.

layers are of the liquid expanded type (cf. Fig. 5). Mixtures containing the two stereoisomers in different proportions gave results identical with those of the pure compounds.

The diastereoisomeric 7-keto-acids, which are intermediates in the synthesis of the 2,9-dimethyltetracosanoic acids¹, differ, as would be expected, in the monolayer behaviour from the latter. On barium substrate at 5° (Fig. 6) force-area curves of the two diastereoisomers differ over the whole range, but both keto-acids give comparatively high pressures out to large areas. Although the force-area curves of the two diastereoisomers are not identical over any part of the curve, the collapse pressures are the same. At 20° the force-area curves for the keto-acids on barium substrate (Fig. 7) and on acid substrate (Fig. 8) are similar in appearance and of the liquid expanded type. The curves for the two diastereoisomers are identical over the expanded region, but after the transition to the condensed state sets in, the force-area curves begin to differ from each other.

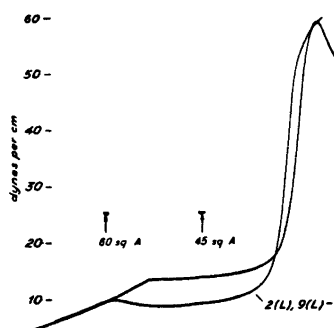


Fig. 7. Force-area curves for the stereoisomeric keto-acids on barium substrate at 20.0°.

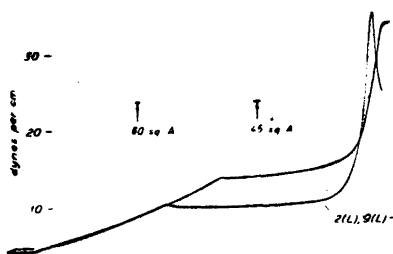


Fig. 8. Force-area curves for the stereoisomeric keto-acids on 0.01 N HCl substrate at 20.0°.

DISCUSSION

The identical monolayer behaviour of the two diastereoisomers of 2,9-dimethyltetracosanoic acid under the conditions investigated indicates that the monolayers are true liquids. The same applies to the keto-acids over the expanded region, but the fact that in this case the force-area curves become different as soon as the transition to the condensed state sets in, in our opinion indicates that the condensed monolayers are more organized than a liquid.

The results suggest that the nature of phase transitions in monolayers may in certain cases be studied with the use of diastereoisomers.

The curves in Figs. 1—3 also show the precision obtainable with the recording mikrokator balance. The largest differences found between the force-area curves of the two 2,9-dimethyltetracosanoic acids, both with regard to pressure and area values, are of the order of 0.3 %. This includes the weighing out of the acids, pipetting out the spreading solvent, the spreading by means of the Agla syringe, and the reproducibility of the balance in the area and pressure recordings. Impurities in the acids would of course also contribute to the error, and the results can therefore also be regarded as a check of the purity of the compounds used. It should be pointed out that the results in Figs. 1—8 have not been especially picked out from a series of recordings showing much greater variations. The three pairs of curves reproduced in Figs. 1—3 were obtained in strict succession, the temperature being changed after each double run.

SUMMARY

The monolayer behaviour of the two dextrorotatory diastereoisomers of 2,9-dimethyltetracosanoic acid has been studied. The acids give identical monolayer force-area curves. The corresponding 7-keto-acids, on the other hand, show identical force-area curves over the expanded region, but as soon as the transition to more condensed forms sets in, the force-area curves begin differ from each other.

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