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C₁₈ FATTY ACIDS. II. THE RELATION OF OLEIC AND ELAIDIC ACIDS TO THEIR HALOGEN ADDITION PRODUCTS.

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One of the most interesting problems in the chemistry of vegetable oils, is the question of the exact constitution of the linolic acids which they contain. Assuming, as is not improbable, that in most¹ oils the acids of the formula C₁₈H₃₂O₂ have their double bonds in the same position, there are nevertheless 4 possible space-isomers (*cis-trans*), and at least two, or perhaps more, of these seem to occur mixed together in each of the commoner oils.²

Although at least 2 tetrabromo-stearic acids, and probably 2 tetrahydroxy-stearic acids, have been obtained as derivatives of ordinary "linolic" acid, there is at present no evidence known to the writer which relates a particular tetrabromo acid to a particular tetrahydroxy acid, or which indicates definitely the spatial structure of any one of these derivatives. Takahashi² has shown that each of the known tetrabromo acids, when reconverted into linolic acid and again brominated, gives a *mixture* of tetrabromo-stearic acids, in substantially the same proportions as are obtained in brominating the fatty acids of the common oils containing linolic acid. It is therefore evident that a rearrangement has taken place, either in the removal of the bromine to regenerate the double bonds, or in the subsequent addition of bromine to the products thus obtained. Incidentally, as this is the only known method of preparing substantially pure "linolic" acid, it becomes doubtful whether anyone has ever prepared this substance in a form which was not a mixture of at least two, and perhaps more, of the possible isomers.

The present paper describes an attempt, which was unsuccessful, to decide whether this rearrangement took place in the removal, or in the addition of bromine. As there is at present no good method of identifying linolic acid except by the preparation of saturated derivatives,³ the elimination of bromine from dibromo-oleic and -elaidic acids and its re-addition were studied, as likely to be similar to the corresponding reactions of linolic acid. Lewkowitsch⁴ states that oleic acid dibromide, on heating with zinc and alcoholic hydrochloric acid, regenerates oleic acid. It was felt, however, that this result required confirmation, in view of the

¹ For tung oil, at least, this not the case.

² *E. g.*, Takahashi, *J. Tokyo Chem. Soc.*, **40**, 233-89 (1919); *C. A.* **13**, 1583 (1919).

³ A search is at present being made for suitable solid derivatives.

⁴ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Macmillan and Co., London, 1913, Vol. I, p. 184.

known behavior of linolic acid and of the fact that both oleic acid and the two dibromides (oleic and elaidic) are liquids or very low-melting solids, and the identification of the products could accordingly scarcely have been very definite.

In order to obtain more definitely characterizable products, the solid anilides of oleic and elaidic acids were used. The dibromides were obtained both by adding bromine to the anilides in chloroform solution, and by brominating the free acids and subsequently preparing the anilides from the brominated products. The compounds obtained by the two methods were identical.

When oleic acid was converted into the dibromide, treated in the usual way with zinc and alcoholic hydrochloric acid to regenerate the double bond, and then again brominated and converted into the anilide, the only product that could be isolated was oleic-anilide dibromide. As the corresponding elaidic-anilide dibromide is much less soluble, and has a higher melting point, it should have been very easy to recognize, even in rather small amounts, if formed. It is accordingly evident that no elaidic acid was formed.

Similarly, when elaidic-anilide dibromide was boiled with zinc and alcoholic hydrochloric acid, only elaidic anilide was obtained.

It is therefore apparent that when the double bond is regenerated in the dibromides of oleic or elaidic acid (or their derivatives) the original acid is re-formed, without appreciable quantities of the isomeric acid. The cause of this difference between oleic and linolic acid derivatives is still unexplained.

Experimental Part.

Oleic-anilide Dibromide.—Fourteen g. of olive oil fatty acids was dissolved in 30 g. low boiling ligroin, and treated with 1 mol. of bromine in the same solvent, cooling in tap water. The solution was heated on the water-bath for some time with 1 mol. of phosphorus pentachloride, and the phosphorus oxychloride and ligroin were distilled under reduced pressure. The residue was added to 2.5 mols. of aniline, and after standing for some time, the excess of aniline and aniline hydrochloride were removed by washing with dil. hydrochloric acid and with water. The product was crystallized from alcohol after treatment with charcoal. After 6 crystallizations, it melted at 60–62°. Purification from ligroin was considerably more effective, the product melting finally at 67°, after softening at 63°. A sharp melting point could not be obtained.

Analysis (Carius). Calc. for dibromo-oleic-anilide: Br, 30.9. Found: 30.0.

The same substance was rather more readily obtained by treating oleic-anilide in 4 parts of chloroform, with 1 mol. of bromine, evaporating the chloroform, and recrystallizing from ligroin. It softened at 64° and melted at 67°, and a mixture of the two products behaved in exactly the same way. It is very soluble in hot alcohol, moderately soluble in the cold, and readily soluble in warm ligroin.

Bromination of Oleic-anilide in Other Solvents.—Oleic-anilide in 7 parts of ligroin was treated with 1 mol. of bromine, also dissolved in ligroin. The anilide was not entirely soluble, and apparently an excess of bromine reacted with the soluble portion.

A small amount of a product melting after recrystallization from alcohol at 90–91° was obtained. It was only slightly soluble in cold alcohol, and separated from it as an almost gelatinous mass without apparent crystalline structure. It was, however, readily reduced to a dry powder. The quantity obtained was not sufficient for analysis.

When oleic anilide was treated at room temperature, in chloroform solution, with 4 mols. of bromine (calc. for oleic-tribromo-anilide dibromide), and the solution washed with sodium hydrogen sulfite solution to remove a slight excess of bromine, a different product was obtained, readily soluble in hot alcohol, moderately soluble cold, and melting at 77–78°.

Analysis (Carius). Calc. for dibromo-oleic-anilide: Br, 30.9. Calc. for dibromo-oleic-monobromo-anilide: Br, 40.2. Found: 37.15.

The analysis shows the product to be a mixture, and less highly brominated than might have been expected.

Elaidic-anilide.—This compound was readily prepared by heating 20 g. of elaidic acid and 15 g. of aniline at 200° for 3 hours in a bomb tube. On recrystallizing from alcohol, the bulky mass of crystals retains an unusually large amount of solvent, so that 3 or 4 crystallizations are necessary. The pure substance melts at 72°, and is readily soluble in hot benzene, moderately soluble cold, very soluble even in cold chloroform, and only slightly soluble in low-boiling ligroin.

Elaidic-anilide Dibromide.—This was made in chloroform solution in the same way as the corresponding oleic acid derivative. It is very soluble in chloroform, readily soluble in hot alcohol, slightly soluble cold; and very soluble in hot benzol. The pure substance melted at 88°.

Analysis (Carius). Calc.: Br, 30.90. Found: 31.45.

The same substance was obtained as follows. Elaidic acid was converted into the chloride by warming with 1 mol. of phosphorus pentachloride, and the phosphorus oxychloride distilled under reduced pressure. The chloride was taken up in chloroform, 1 mol. of bromine added (with moderate cooling), and after a few minutes, an excess of aniline. The product, after recrystallization from alcohol, was identical with that described above.

Oleic Acid Regenerated from Oleic Dibromide.—Twenty g. of oleic acid was brominated in chloroform in the usual manner. The chloroform was distilled and the residue heated for 8 hours under a reflux condenser with an excess of zinc and alcoholic hydrochloric acid. The unsaturated acid thus formed was separated, dried, and converted into the chloride with phosphorus pentachloride, the oxychloride formed being removed under reduced pressure. The chloride was taken up in chloroform and re-brominated, then treated with an excess of aniline. No elaidic-anilide dibromide could be isolated (although it is less soluble and higher melting than the product obtained) the only product isolated being oleic-anilide dibromide, melting, after 3 recrystallizations from ligroin, at 65°.

Elaidic-anilide from Elaidic-anilide Dibromide.—Four g. of the dibromide was refluxed for 8 hours with zinc and alcoholic hydrochloric acid. The resulting product was separated and heated for 2 hours with alcoholic potash with the intention of completing the hydrolysis of the anilide. Even after this treatment, however, most of the anilide had resisted hydrolysis. Recrystallized from alcohol and then from ligroin, the elaidic-anilide melted at 67° and was shown by mixing with pure elaidic-anilide to be identical with that substance.

Summary.

1. The anilides of oleic and elaidic acids and their dibromides have been used to demonstrate definitely that there is no *cis-trans* isomerization

