The Nature of Smit's Linoleic Acid Isomer. 8t,10t-Octadecadienoic Acid

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CONJUGATED unsaturated fatty acids have gained increased interest since the introduction of artificially conjugated oils in the paint and varnish industries. The two best known representatives of conjugated dienoic acids are Mangold's 9,11-octadecadienoic acid (3) and the 10,12-isomer described by the author (4, 5).

Another conjugated linoleic acid has been isolated by Smit (10) in the course of extensive investigations on unsaturated fatty acids carried out with Böeseken at Delft, Holland. This acid, melting at 56°, was obtained by him upon debrominating a tetrabromostearic acid melting at 124°, which in turn resulted when he brominated the distillate of castor fatty acids. This distillate, first described by Krafft (2) and Mangold (3), is essentially the dehydration product of ricinoleic acid and was subsequently reesterified by Scheiber (7) in his well-known process for the production of dehydrated castor oil.

Smit and Böeseken assigned to their new acid the structure of a 9,11-acid like that of Mangold's product but thought it to be still further elaidinated because of its observed greater stability towards oxidation agents and halogen solutions (11).

While the work of the Dutch chemists left no doubt as to the conjugated nature of their new acid, they gave no proof of the position of the double bond system. Serious doubt in the structure assigned by them to the new acid was raised by the realization that Mangold's acid already was completely elaidinated, i.e., the trans,trans-isomer. This was confirmed by the observation that Mangold's acid yields theoretical diene values without activation whereas isomers with partial or entire cis-structure show stearic hindrance in diene synthesis according to a recent study by the author (6).

Smit's acid would then have to be either an incompletely elaidinated 9,11-acid, which in view of its high melting point was very unlikely, or the conjugated system should have a different position in the fatty chain. The latter alternative would be quite surprising, considering the origin of the tetrabromide. Since ricinoleic acid has its double bond fixed between the 9th and 10th carbon of the chain, its distillation product up to the present was considered to consist of 9,11- and 9,12-acids.

Thus it was recently suggested (9) that Smit's acid might be identical with the 10,12-linoleic acid melting at 57°, which however, as we have pointed out (4), forms no bromide melting at 124°. In any event the question was thought worth investigating, and it turned out that the acid in question is 8,10-octadecadienoic acid, which like the two above mentioned conjugated linoleic acids, has the trans,trans-structure.

Summary of Experimental Work

The castor fatty acids were distilled according to Scheiber (7). The distillation product had a Woburn iodine value of 163.8, pandiene value (6) of 33.2, and n_D^{25} 1.4750. Treating of the distillate with an excess of bromine in petrolether at −20°C. resulted in 8.4% of their weight of solid bromides, m.p. 98-108° C. When purified ricinoleic acid was the starting material, the distillate ($n_D^{25} = 1.4770$, pandiene value 41.0) yielded 12.6% of solid bromides. Smit reported a yield of 3% melting at 124°, 3.5% melting at 113°, and a further crop melting below 90°. After some fractionation and recrystallization from acetone and heptane a tetrabromide fraction melting sharply at 123-124° was obtained. Upon treatment with zinc in ether containing some HCl a semi-solid fatty acid resulted, about one-third of which melted sharply at 55.5 to 56.5° upon recrystallization from dilute alcohol. A further tetrabromide fraction melted between 100 and 120° and upon similar treatment yielded mixtures of the same acid with another solid linoleic acid—probably Mangold's acid—which could not be separated by crystallization due to mixed crystal formation. The new solid acid depressed the melting points of 9t,11t-linoleic acid from 54° to 44° and of 10t,12t-acid from 57 to 45° when tested by Kofler's contact method (1).

Observed constants were:

Diene value	89.8 (calc. 90.5)
Pandiene value (6)	91.1 (calc. 90.5)
Total iodine value (Woburn)	181.5 (calc. 181.0)
Partial iodine value (short Wijs)	90.4 (calc. 90.5)
Diene value by difference	91.1 (calc. 90.5)
Refractive index (n_D^{60})	1.4682
Density (60°)	0.8808
Molar refraction	88.53
Exaltation	2.63

Oxidation with permanganate in acetone solution led to the isolation of a dibasic acid as major product which melted at 142-143° and showed no depression with genuine suberic acid, with which it could be shown to be identical by the micro-methods of Kofler (1). From this the position of the double bond closest to the carboxyl group is between the 8th and 9th carbon atom while the iodometric and dienometric behavior, which was typical for a conjugated diene, fixed the position of the second double bond between the 10th and 11th carbon atom. The identity of diene value and pandiene value is considered sufficient proof of the trans,trans-structure in view of the arguments published elsewhere (6).

The maleic anhydride addition product after recrystallization from ether with little added petrol ether melted sharply at 110°, i.e., higher than the corresponding products from the above-mentioned 9,11- and 10,12-acids; these melt at 94° and 102°, respectively. Identification of the various dienoic acids by means of their maleic anhydride adducts was found to be very convenient as these show characteristic crystal properties under the microscope.

On brominating the 8,10-linoleic acid in the dark, the resulting product melts around 126° while in the light a tetrabromide melting sharply at 160-161° after crystallization from acetone is obtained. The identical bromide (m.p. 159-160.8°) is also formed when the distilled ricinoleic acid itself is treated with an excess of free bromine in the light indicating that 8,10-linoleic acid is present in the distillate from the beginning and is not merely formed during the bromination or debromination procedure.

A liquid fatty acid fraction, which is obtained along with the solid acid upon debrominating the tetrabromide of m.p. 124°, gave almost theoretical pandiene values (83.1) but lower diene values (43.1), showing the presence of cis-structure. Its addition product with maleic anhydride was identical with that of the solid acid, and treatment of the liquid acid with a trace of iodine yielded a further crop of the solid isomer.

Comparison and Discussion

Contrary to the distilled castor fatty acids, a dehydrated castor oil prepared with sodium bisulfate according to Ufer (12) gave no solid bromide with a melting point of 124° or thereabout. Thus 8,10-octadecadienoic acid seems to be a specific product formed upon dehydrating ricinoleic acid by distillation, indicating a much more complicated reaction than has so far been assumed. Differences in the behavior of dehydrated castor oil made catalytically on one hand and by the Scheiber process of distillation on the other have also been observed upon alkali isomerization (5).

Scheiber (8) states that he has found suberic acid before among the oxidation products of the distillate but had believed them to be due to secondary oxidation of azelaic acid derived from 9,11-linoleic acid. To explain the present observation he suggests that dehydration may take place between the hydroxyl group and a hydrogen atom from the 8th carbon atom in the chain leading either first to an unstable pentene-ring or directly to an 8,12-biradical which is stabilized by a hydrogen shift from the 11th to the 12th carbon forming the diene system. The latter mechanism seems reasonable although experimental proof is lacking for the present.

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ABSTRACTS

Don Whyte, Editor

• Oils and Fats

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Factors affecting flavor stability of soybean oil. Anon. *Soybean Digest* 11(12), 16(1951). A list is given of the factors in processing and refining which favorably and unfavorably affect the flavor stability of soybean oil.

Fat splitting tower at Swift & Co. has achieved efficiencies over 99%. Anon. *Chem. Proc.* **15**(1), 50(1952). A brief description.

The component acids of the perinephric and interscapular fats of a rabbit. G. Clement and M. L. Meara (Univ. Liverpool). *Biochem. J.* **49**, 561(1951). The component fatty acids of perinephric fat are (mole %) lauric 0.5, myristic 6.5, palmitic 31.9, stearic 4.7, hexadecenoic 5.7, hexadecadienoic 0.2, hexadecatrienoic 0.3, oleic 30.4, linoleic 15.6, linolenic 3.1 and unsaturated C_{20-22} 1.2. The interscapular fat has a similar composition but contains about 4% more oleic acid and 4% less linoleic acid. Both fats were broadly similar to those of other tame rodents.

Human fecal lipids. D. C. Edwards and R. P. Cook (Univ. College, Dundee). *Biochem. J.* **49**, xli(1951). The lipids extracted from dried human feces contained 34% unsaponifiable matter (⅓ of which are sterols), 29% volatile fatty acids and 37% non-volatile fatty acids. The latter contain 25% petroleum ether (40-60°) insolubles, 47% solid acids and 29% liquid acids. Oleic acid is the main component of the liquid acids; the solid acids contain myristic, palmitic, stearic and higher acids.

The constitution of hexadecatrienoic acid from the glycerides of rape (Brassica napus L.) leaf. J. K. Heyes and F. B. Shorland (Dept. Sci. Ind. Res., Wellington, N. Z.). *Biochem. J.* **49**, 503(1951). Oxidation with $KMnO_4$ in acetone of methyl hexadecatrienoate isolated from rape-leaf glycerides yielded pimelic, oxalic and propionic acids. This evidence in association with spectroscopic results before and after isomerization show that this acid has the formula

$$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_5COOH$$

The polymorphism of n-hexadecanol and n-octadecanol. D. G. Klop and E. S. Lutton (Procter & Gamble Co.). *J. Am. Chem. Soc.* **73**, 5593(1951). The polymorphism of n-hexadecanol and n-octadecanol has been studied by x-ray diffraction and thermal data. Three forms have been found. The α form melts at the freezing point and exists as a meta stable form in a narrow temperature range near the m.p. In this temperature range gradual transformation to the stable β form occurs. Cooling the α form causes abrupt transformation to the sub-α form, which also changes gradually to β on aging. Only one m.p. has been found for each of the alcohols studied.

Autoxidation of methyl esters of peanut oil fatty acids. The effects of incubation temperature and of added iron on infrared absorption spectra and on other changes. H. W. Lemon, Elizabeth H. Kirby and Ruth M. Knapp (Ontario Res. Found., Toronto, Ont.). *Can. J. Tech.* **29**, 523(1951). The infrared absorption spectra of methyl esters of peanut oil fatty acids showed changes principally in three regions during heating in air at 22°-100°. In the –OH stretching region (3730-3005 cm^{-1}) a band developed during the early stages of autoxidation which was believed to be associated with the formation of hydroperoxides. Later two bands, probably associated with the decomposition of hydroperoxides to other compounds containing hydroxyl groups, appeared at higher wave numbers. Increased temperature of incubation accelerated the formation and decomposition of hydroperoxides, and the presence of iron stearate catalyzed only their decomposition.

Procedure for the microestimation of nitrogenous phosphatide constituents. Celia Levine and E. Chargaff (Columbia Univ., New York City). *J. Biol. Chem.* **192**, 465(1951). The separation of chromatography on filter paper and the quantitative estimation of minute amounts (5-75 γ) of ethanolamine, serine and choline are described. Analysis of the phospholipids from beef brain indicated the presence of several novel nitrogeneous compounds but they were not identified.

The polymorphism of the disaturated triglycerides—OSS, OPP, POS and OSP. E. S. Lutton (Procter and Gamble Co.). *J. Am. Chem. Soc.* **73**, 5595(1951). Two groups of disaturated triglycerides have been studied, (1) the unsymmetrical diacid compounds—1-oleyldistearin (OSS) and 1-oleyldipalmitin (OPP) and (2) the triacid compounds—2-oleylpalmitylstearin (POS), 2-palmityloleylstearin (OPS) and 2-stearyloleylpalmitin. All 1-oleyl compounds are β'-3 stable from solvent; OSS and OPP also give β'-3 as stable form from melt; OPS gives sub-β'-3; OPS gives β'-2. All 2-oleyl compounds (POS, SOS and POP) are β-3 stable from solvent and melt. OSS, OPP and SOS exhibit α-3 forms at the lowest m.p., while POS, OPS and POP show α-2, but OSP shows sub-α-2. The highly individualistic behavior should serve as a basis for identifying predominant disaturated components of many natural fats.

Studies on degradation of fats by microorganisms. I. Preliminary investigations on enzyme systems involved in the spoilage of fats. S. Mukherjee (Univ. Calcutta). *Arch. Biochem. Biophys.* **33**, 364(1951). The first step in the rancidification of