

[CONTRIBUTION FROM THE KENT LABORATORY, UNIVERSITY OF CHICAGO.]

C₁₈ FATTY ACIDS. I. THE NON-IDENTITY OF ELEOSTEARIC ACID TETRABROMIDE FROM TUNG OIL WITH ORDINARY LINOLIC ACID TETRABROMIDE.¹

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Kametaka² brominated crude tung oil fatty acids in glacial acetic acid, and obtained a tetrabromo-stearic acid which melted, after purification, at 114°. The same product was obtained when pure α -eleostearic acid was first isolated from the crude acids, and then brominated. The yield is not stated, but perhaps a small yield is implied in the remark that the amount of product obtained on brominating the pure acid was not sufficient for analysis. As ordinary linolic acid, from cottonseed or other common oils, gives with bromine a tetrabromo-stearic acid of this same melting point, Kametaka concludes that the two tetrabromides are identical, and that the two unsaturated acids are, therefore, obviously stereoisomers. This idea is supported by the fact that on oxidizing α -eleostearic acid, it is possible to isolate a tetrahydroxy-stearic acid melting at 171° to 172°, which is approximately the melting point (173° to 174°) of the rather difficultly purified sativic acid obtained by oxidizing ordinary linolic acid. Such an authority as Lewkowitsch³ specifically accepts the identity of the two tetrabromides as proved by these considerations.

It is not, however, recorded that this supposed identity of the tetrabromides was confirmed by the determination of the melting point of a mixture of the two compounds, and workers in this field must have been struck by two facts which make the above assumption doubtful. The first of these is the strong tendency of α -eleostearic acid to crystallize, whereas linolic acid has resisted all efforts—and there have been many—to obtain it in solid form; this might of course be due to the fact that "linolic" acid is ordinarily a mixture of two or more stereoisomers,⁴ whereas α -eleostearic acid *might* conceivably be a pure substance. The second is that, with a molecule of this size, it is not at all impossible that two isomers should show even in two of their derivatives, remarkable similarities in physical properties, without being identical.

These considerations led the writer to a further investigation of the question. The bromination of pure α -eleostearic acid from tung oil (solidification point 48°) in glacial acetic acid, gave only a 5% yield of solid product (which accounts for Kametaka's remark quoted above) and this

¹ Presented at the Chicago Meeting of the American Chemical Society, September, 1920.

² Kametaka, *J. Chem. Soc.*, **83**, 1042 (1903).

³ Lewkowitsch, "Chemical Technology of Oils, Fats, and Waxes," 5th Ed., **1913**, I, p. 201.

⁴ K. Takahashi, *C. A.* **13**, 1583 (1919).

when pure melted at 115°, and is accordingly identical with the product obtained by Kametaka. With the corresponding tetrabromide of linolic acid from cottonseed oil (m. p. 114°) a mixture was obtained which softened at 100°, and liquefied at 103°. Furthermore, ethyl tetrabromo- α -eleostearate, m. p. 50°, was prepared, and its melting point was found to be lowered by admixture of ethyl tetrabromo-linolate (m. p. 63°).¹ The two tetrabromides are, therefore, not identical, but isomeric, and there is thus no evidence that the two acids are space-isomers.

On account of solubility relations, it is customary to brominate linolic acid in low boiling ligroin. It is noteworthy that when an insufficient amount of bromine is used under these conditions, only the tetrabromine is formed, the excess of acid being unaffected. On attempting to brominate α -eleostearic acid in this solvent, there was obtained a fair yield (about 50%) of a dibromide (m. p. 85°) as the only solid product. This behavior is further evidence of the difference between the α -eleostearic acid of tung oil, and ordinary linolic acid. By using a considerable excess of bromine, a certain amount of tetrabromide can be formed in ligroin solution; and the dibromide can be converted into tetrabromide by further bromination in acetic acid.

Incidentally, β -eleostearic acid (m. p. 71°) gave in acetic acid a tetrabromide, m. p. 115° (previously prepared by Morrell)² which was shown by determination of the melting point of a mixture, to be identical with the tetrabromide of α -eleostearic acid. The yield from the β -acid is somewhat better; but in both cases it is obvious that *other* tetrabromides are formed, as is the case also with linolic acid.

Experimental Part.

Preparation of α -Eleostearic Acid from Tung Oil.—Sixty g. of sodium hydroxide was dissolved in 75 cc. of water, added to 600 cc. of alcohol, and mixed with 300 g. of tung oil with shaking. The mixture was heated on the water-bath for an hour under a reflux condenser, and shaken well until it became solid. Saponification was then complete, and the fatty acids were liberated by adding 2 liters of hot water containing an excess of sulfuric acid, and continuing the heating. The crude acids solidified at 33.5°. For recrystallization, they were dissolved in half their weight of alcohol, and chilled slightly. After two such recrystallizations, the solidification point was 48°. The beautifully crystalline acid must be used within a day or two of its preparation, unless specially protected from oxidation by air.

α -Eleostearic Acid Dibromide.—To a solution of 10 g. α -eleostearic acid in 100 g. of low-boiling ligroin (a temperature of 25° is necessary to keep it in solution) was added slowly 3.8 cc. (4 atoms) of bromine. The solution decolorized instantly, and on chilling deposited 5.8 g. of solid. On adding bromine to the filtrate until a permanent color was obtained (3 cc. was required; the ligroin evidently contained ethylene hydrocarbons) and again chilling, an additional 4 g. of dibromide was obtained. The product, recrystallized from high-boiling ligroin, melted at 85° to a clear oil, which blackened on

¹ L. S. Palmer and P. A. Wright (*J. Ind. Eng. Chem.*, 6, 822 (1914)) give 58–8.5° as the m. p. of ethyl tetrabromo-linolate.

² Morrell, *J. Chem. Soc.*, 101, 2082 (1912).

being held a short time at this temperature. The pure substance discolors noticeably on 24 hours' standing, and in the course of a few days becomes completely black. It is readily soluble in cold alcohol or benzene, and in hot high-boiling ligroin, but difficultly soluble in low-boiling ligroin.

Analysis: Calc. for $C_{18}H_{32}O_2Br_2$: Br, 36.31. Found: (Carius), 36.32.

α -Eleostearic Acid Tetrabromide.—A solution of 20 g. of α -eleostearic acid in 100 g. of glacial acetic acid was cooled until the acid just failed to separate, (5° to 10°) and 4 equivalents of bromine added. A decided bromine color persisted, and on chilling 2 g. of solid, m. p. 108° , separated, and was recrystallized from high boiling ligroin until it melted constantly at 115° . No more solid could be obtained from the mother liquors, and the fate of the remaining 95% of the material is as yet undetermined. This solid product seems, however, to be identical with Kametaka's α -eleostearic acid tetrabromide prepared similarly. Mixed with linolic acid tetrabromide (m. p. 114°) from cottonseed oil, it softened at 100° and melted at 103° ; the two products are evidently different.

The same product was obtained when the dibromide of α -eleostearic acid was dissolved in acetic acid and treated with the theoretical quantity of bromine.

Bromination of β -Eleostearic Acid.— β -Eleostearic acid was prepared by the method of Morrell. Brominated in the same manner as the α -acid, it gave Morrell's tetrabromide, m. p. 115° . This was shown by the mixed-melting-point test to be identical with the α -tetrabromide.¹

Calc. for $C_{18}H_{32}O_2Br_4$: Br, 53.3. Found: (Carius), 53.7.

Ethyl α -Eleostearate Tetrabromide.—The α -tetrabromo acid was esterified in the usual manner. The ester was readily soluble in ligroin and in alcohol. Crystallized from the latter, it melted at 50° . (Ethyl linolate tetrabromide m. p. 63° .)

Summary.

The tetrabromide of α -eleostearic acid is not identical with that of linolic acid, as has previously been supposed. It is therefore no longer necessary to assume that α -eleostearic and linolic acids are space isomers.

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¹ As iodine powerfully catalyzes the rearrangement of α -eleostearic acid to the β -acid, it seems likely that the tetrabromide in question is really that of the β -acid. An attempt is being made to settle this point.