

On the Constitution of the so-called Elæomargaric Acid.

By

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I showed three years ago (Jour. of the College of Science, Imperial University of Tokyo, Vol. XIX., Article 12; Jour. Chem. Soc., 1903, 83, 1042-1045) that the composition of the so-called elæomargaric acid is neither $C_{17}H_{30}O_2$, as given by its discoverer CLOËZ (Compt. rend., 1876, 83, 943.) nor $C_{18}H_{30}O_2$, as asserted by L. MAQUENNE (Compt. rend., 1902, 135, 696-698); but that it must be $C_{18}H_{32}O_2$, isomeric with linolic acid. Since then I have continued the work with the object of determining, if possible, the constitution of the acid. Unfortunately, no definite conclusion on this point has yet been reached; but in view of the fact that circumstances will prevent me from continuing the work for some time, I propose to describe some of the results thus far obtained.

With regard to the constitution of elæomargaric acid, CLOËZ's own words are as follows:—

„L'acide élæomargarique est un homologue supérieur des acides sorbique, linoléique et palmitolique; il se place entre ce dernier et l'acide stéarolique, obtenu artificiellement par l'action de la potasse sur l'acide oléique bromé.” (*loc. cit.*).

L. MAQUENNE, who, as above stated, regards the composition

of the acid as $C_{18}H_{30}O_2$, observes that azelaic acid ($C_9H_{16}O_4$) and n-valerianic acid are formed by the oxidation of the acid as well as its stereoisomer elæostearic acid, and states :—

„Le reste de la molécule, qui comprend encore 4^{at} de carbone, est entièrement détruit, ce qui laisse indecise la question de savoir si l'acide élæostéarique renferme deux ou trois liaisons multiples ; en d'autres termes, s'il est éthylénique et acétylénique ou triéthylénique.

Le seul fait certain qui découle des résultats précédants c'est que l'acide élæostéarique possède deux lacunes dans les positions 5 et 9." (*loc. cit.*).

Now, according to O. DOEBNER (Ber., 1890, 23, 2374), sorbic acid $CH_3-CH=CH-CH=CH-CO_2H$ and other acids containing the group $-CH=CH-CH=CH-CO_2H$ when oxidised with potassium permanganate in a slightly alkaline solution give tartaric acid among other products ; but on oxidising elæomargaric acid in the same manner, it was found that no tartaric acid was produced. It appears, therefore, that the statement by CLOËZ that elæomargaric acid is a homologue of sorbic acid is not founded upon fact. Moreover, elæomargaric acid, unlike stearolic acid, and behenolic acid, does not give a definite product with conc. sulphuric acid. CLOËZ's idea that elæomargaric acid is a homologue of stearolic acid and contains a triple bond is, therefore, also rendered improbable.

Further, on repeating MAQUENNE's oxidation process, a large quantity of azelaic acid was indeed obtained, but the presence of n-valerianic acid could not be established with certainty. There seems, therefore, to be no doubt that one double bond out of the two, which elæomargaric acid doubtless contains, is in the middle of the chain of 18 carbon atoms. As to the position

of the other double bond no definite conclusion can be drawn at present; but in view of the fact that many unsaturated acids, which give azelaic acid $\text{CO}_2\text{H}(\text{CH}_2)_7\text{CO}_2\text{H}$, on oxidation; such for example as oleic acid and stearolic acid, contain the group $=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$ or $\equiv\text{C}(\text{CH}_2)_7\text{CO}_2\text{H}$, it appears probable that it is on that side of the middle double bond which is further removed from the carboxyl group. The result of the action of aniline upon elæomargaric acid, as described further on, favours this view.

Experimental.

Oxidation of elæomargaric acid with potassium permanganate.

Following the method of oxidation described by DOEBNER (*loc. cit.*), 10 gr. of elæomargaric acid was dissolved in caustic potash sufficient for its neutralisation, diluted with water to 2 litres, and cooled to 2–3°. To this solution, 18 gr. of potassium permanganate dissolved in 2 litres of water and cooled to 2–3° was gradually added. After standing for 3 hours the precipitate of manganese dioxide was filtered off, and the filtrate concentrated to $\frac{1}{2}$ litre and acidified with hydrochloric acid, when a brown precipitate was formed, which was collected and recrystallised several times from alcohol. In this manner, a white crystalline substance of m. p. 130° was obtained, which, from the determination of the acid equivalent by means of standard baryta water, proved to be dihydroxystearic acid.

The filtrate from the impure dihydroxystearic acid was rendered slightly alkaline with ammonia, and calcium chloride added, when a white precipitate was formed. This apparently consisted of calcium oxalate, and no tartaric acid could be detected.

The oxidation process was repeated, not, however, at low temperatures as before, but at an ordinary temperature (about 12°). In this case, azelaic acid (m. p. 105°) was formed, besides dihydroxystearic acid, but again no tartaric acid was obtained.

As the formation of dihydroxystearic acid $C_{18}H_{34}(OH)_2O_2$ by the oxidising action of potassium permanganate upon elæomargaric acid $C_{18}H_{32}O_2$, i. e. by a mere addition of $2H_2O$, appeared somewhat strange, I next tried HAZURA'S method of oxidation, the elæomargaric acid used having been carefully recrystallised from alcohol and made free from accompanying oleic acid. Here again dihydroxystearic acid was obtained, besides azelaic acid and an unknown substance of a white crystalline nature, m. p. $123-125^{\circ}$, soluble in water and alcohol, but insoluble in ether. Saticic acid was not formed. This was probably due to the high temperature employed and the decomposition of saticic acid once formed into azelaic acid. Lastly, elæomargaric acid was oxidised by MAQUENNE'S method (Bull. soc. chim., 1899, 3^e série, 21, 1061) on a water-bath; a large quantity of azelaic acid was obtained, but no n-valerianic acid could be detected in the mother liquor.

*Action of concentrated sulphuric acid upon
elæomargaric acid.*

Following the method, by which the constitutions of behenolic and stearolic acids were determined (J. BARUCH, Ber., 1893, 26, 839; 1894, 27, 172), elæomargaric acid was mixed with 5 times its weight of pure conc. sulphuric acid; heat was evolved and the smell of sulphur dioxide perceived, the crystals of elæomargaric acid melting into a dark liquid. After standing for

3 4 hours, the liquid was poured into a large quantity of water, when a greenish-blue resinous mass was obtained, which could not be crystallised either from alcohol, acetic acid, acetic ester, or other solvents. This negative result may perhaps be taken as showing that elæomargaric acid differs from behenolic and stearolic acids in not containing a triple bond.

Fusion of elæomargaric acid with caustic potash.

Crystallised elæomargaric acid was fused with about four times its weight of solid caustic potash, in a nickel or iron crucible, at about 400° for 3-4 hours. A part of the acid floated on the surface of the fused mass and did not quite dissolve. The dark coloured mass obtained on cooling was extracted with water, filtered, and acidified with hydrochloric acid, when a small quantity of a brown substance separated, which, after repeated recrystallisation from alcohol, gave a white crystalline substance, whose melting point was 95-96°. Its acid equivalent was found to be about 515, so that it was not azelaic acid, although its melting point almost exactly agreed with that of the latter. The quantity of the substance was too minute to admit of an elementary analysis.

In another fusion experiment a small quantity of a white crystalline substance, melting at about 58°, was obtained, whose acid equivalent was found to be about 255. It was probably *palmitic acid* ($C_{16}H_{32}O_2 = 256$).

Reaction between elæomargaric acid and aniline.

According to W. AUTENRIETH and C. PRETZELL (Ber., 1903, 36, 1262) unsaturated monobasic acids of the olefine series, in

which the double bond is between the $\alpha\beta$ or $\beta\gamma$ carbon atoms, react with aniline and form not only anilides but also aniline addition products.

Following their method and with the object of seeing whether elæomargaric acid gives analogous compounds, about 10 grammes of the pure acid and an equal weight of freshly distilled aniline (about 3 mol.) were heated together in a small flask on an oil-bath to 180–190° for 3–4 hours. After cooling, water and dilute acetic acid were added and well shaken in order to remove free aniline; the residual crystalline mass was twice recrystallised from alcohol. White lustrous scaly crystals were thus obtained, which melted at about 80°.

Nitrogen determinations gave the following results:—

0.075 gr. of the substance gave 3 c.c. nitrogen at 6°, 764.4 m.m.

∴ N=4.90%,

0.2445 gr. of the substance gave 8.3 c.c. nitrogen at 3°, 765.4 m.m.

∴ N=4.22%.

Calculated for the anilide $C_{18}H_{31}O.NH.C_6H_5$ N=3.94%.

On keeping these crystals (m. p. 80°) in a desiccator, they became sticky and turned yellow, owing probably to their being not quite pure.

In other experiments, white scaly crystals of m. p. 67° were obtained. These crystals do not change on keeping. Nitrogen determinations gave the following results:—

0.2352 gr. of the substance gave 6.8 c.c. at 10°, 764.7 m.m.

∴ N=3.48%,

0.3298 gr. of the substance gave 10.0 c.c. at 10°, 769 m.m.

∴ N=3.67%.

Mean 3.58%.

The anilide of elæomargaric acid $C_{18}H_{31}O.NH C_6H_5$ requires $N=3.94\%$, while the addition product of the anilide with one molecule of aniline requires $N=6.25\%$.

The product above obtained must therefore be the anilide of elæomargaric acid and is still unsaturated. To the glacial acetic acid solution of the anilide of m. p. 80° , bromine was added drop by drop until the red colour of bromine no longer disappeared; on cooling with ice, a white precipitate was obtained, whose m. p. was found to be about 95° .

The non-formation of aniline addition product may be taken as an indication that the double bonds in elæomargaric acid are not near the carboxyl group.

Esters of elæomargaric acid.

Methyl and ethyl esters of elæomargaric acid were prepared by the usual method. The methyl ester decomposed on warming, becoming dark coloured and giving off a disagreeable odour. But the ethyl ester was stable and of a transparent yellow colour, distilling at $230-240^\circ$ under a pressure of 25 m.m.

From the ethyl ester, a bromine addition-product was prepared by the usual method, which was at first a colourless, transparent liquid, but on standing it gradually became dark coloured.

Since my first paper on elæomargaric acid appeared in 1903, the only literature on this subject which I have been able to find, is a paper by MORITZ KITT (Chem. Rev. Fett- u. Harz-Ind., **11**, 190-191), which, however, I have only seen in abstract

(Chem. Central-Blatt, 1904, II, 949). He seems not to have seen my paper, nor that of L. MAQUENNE (Comp. rend., 1902, 135, 696), as no reference to these papers is made. It also appears that he had obtained no definite results as to the composition or constitution of this acid.

