

The Composition of so-called Elæomargaric Acid.

By

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The oil of *Elaeococca vernicia*, or Japanese wood oil, was first investigated by S. Cloëz (*Compt. rend.*, 1875, **81**, 469 ; 1876, **82**, 501 ; 1876, **83**, 943), who, on saponifying the oil with alcoholic potash, obtained two acids, one of which was solid and the other liquid at the ordinary temperature. At first, he gave the formula $C_{17}H_{30}O_3$ to the solid acid, which he named *margarolic acid*, but in his third paper he changed the formula to $C_{17}H_{30}O_2$, having found that the earlier formula was incorrect owing to some absorption of oxygen by the acid having been overlooked. He also changed the name of the acid to *elæomargaric acid*. The liquid acid, which he at first named *elæolic acid*, was afterwards found to be ordinary oleic acid, the oil containing about 75 per cent. of the glyceride of elæo-margaric acid and 25 per cent. of olein.

From the analysis and the determination of the neutralisation number, K. Ishikawa (*Dissertation*, 1885, unpublished) gave the formula $C_{17}H_{28}O_2$ to the solid acid, whilst De Negri and Sburlati (*L'Orosi*, 1896, **19** 291), adopted Cloëz's formula, $C_{17}H_{30}O_2$.

In 1899, K. Higuchi (*Journ. Chem. Ind., Tokyo*, **2**, 1), by

oxidising the solid acid with potassium permanganate in an alkaline solution, obtained, besides dihydrostearic acid, a product which resembled sativic acid in many respects, but which he did not further examine. Quite recently, L. Maquenne (*Compt. rend.*, 1902, **135**, 696) has published a paper "On the solid acid from the oil of *Elæococca vernicia*," in which he endeavoured to show that the composition of the acid is $C_{18}H_{30}O_2$ rather than $C_{17}H_{30}O_2$ as given by Cloëz, and that the acid must therefore be stereoisomeric with linolenic acid. He arrived at this conclusion merely from the analysis of the acid, and stated that on account of the acid not forming any definite derivatives, its composition cannot be established by indirect means, his attempt to prepare the bromine additive product having failed.

The present communication is a preliminary report of an investigation, begun in 1901 and still in progress, which has for its object the determination of the composition of the acids of the oil by studying their oxidation and bromine additive products.

Although the work is still incomplete, it is desirable, in view of the appearance of Maquenne's paper, that the results should at once be published. A bromine additive product having the formula $C_{18}H_{32}O_2Br_4$ was prepared without any difficulty from the mixture of acids produced by saponifying the oil, and from the recrystallised solid acid were isolated oxidation products having the formulæ $C_{18}H_{32}(OH)_4O_2$ and $C_{18}H_{34}(OH)_2O_2$, but no derivatives of either of the acids $C_{17}H_{30}O_2$ or $C_{18}H_{30}O_2$ could be obtained.* If the acid $C_{18}H_{30}O_2$ had been present in the mixture, as is asserted by Maquenne, the oxidation product, $C_{18}H_{30}(OH)_6O_2$, might have been expected, and should have been obtained in the course of a systematic separation of the products of oxidation (see experimental part). The principal acids of the oil

* In confirmation of the statement that no hexabromide can be obtained, see Walker and Warburton in the *Analyst*, 1902, **27**, 238.

appear, therefore, to be oleic acid and a solid acid having the formula $C_{18}H_{32}O_2$, stereoisomeric with linolic acid, whilst the presence in any considerable quantity of the acid $C_{18}H_{30}O_2$ is excluded. The determination of the neutralisation number of the solid acid by means of carefully standardised alkali shows, moreover, that this corresponds with the formula $C_{18}H_{32}O_2$ rather than with $C_{17}H_{32}O_2$.

No attempt was made to repeat the analyses of the solid acid, since no definite information was to be expected from the result on account of the small difference in the percentage amounts of carbon and hydrogen required by the formulæ $C_{18}H_{32}O_2$, $C_{18}H_{30}O_2$, and $C_{17}H_{30}O_2$. The silver and lead salts of the solid acid were prepared, but they are both amorphous and very readily oxidisable in the air, even more so than the acid itself, so that, although silver estimations were made, no concordant results could be obtained. The reduction of the solid unsaturated acid by heating in a sealed tube with fuming hydriodic acid and red phosphorus has been tried, but the experiments in this direction have not yet been brought to a successful issue.

Experimental.

Saponification of the Oil.—To 30 grams of the cold-drawn oil contained in a flask were added 100 c.c. of alcohol and 15 grams of caustic potash, dissolved in 60 c.c. of water. The flask was connected with an inverted condenser and the contents gently boiled on the water-bath for about two hours. Hydrochloric acid was then added, in slight excess, to the clear alcoholic solution, when a brown oil separated, changing into a crystalline mass on cooling. By recrystallisation from alcohol, the solid acid was obtained in the form of white, lustrous laminae melting at 43—44° (Cloëz gives the melting point of the solid acid as 48°, whilst De Negri and Sburlati give it as 43·8°).

Bromine Additive Product.—Fifty grams of the crude acid were, according to Hazura's method (*Monatsh.*, 1887, **8**, 148), dissolved in 150 c.c. of glacial acetic acid, and to the solution, cooled by means of ice, 21 c.c. of bromine were gradually added with constant shaking; on thoroughly cooling the mixture, a crystalline precipitate separated out, together with some oily matter. After the precipitate had been repeatedly crystallised from glacial acetic acid and alcohol, its melting point was found to be 114° , which agrees with that of the bromine additive product of linolic acid, $C_{18}H_{32}O_2$. The bromine was estimated by Carius' method, with the following results:

I. 0.1830 gave 0.2279 AgBr. Br=53.01.

II. 0.2702 ,, 0.3381 AgBr. Br=53.25.

$C_{18}H_{32}O_2Br_4$ requires 53.33; and $C_{17}H_{30}O_2Br_4$, 54.61 per cent.

On bromination, the pure recrystallised acid also gave a product melting at 114° , but its quantity was too small for a bromine estimation.

Oxidation Products.—30 grams of the crude acid were, again according to Hazura's method (*Monatsh.*, 1888, **9**, 198) mixed with 36 c.c. of caustic potash solution, sp. gr. 1.27, and the soap thus obtained was dissolved in 2 liters of water. To this solution were added, gradually and with constant shaking, 2 liters of 1.5 % potassium permanganate solution and, after standing for 12 hours, the precipitated manganese dioxide was filtered off. The filtrate, on acidifying with sulphuric acid, gave a white flocculent precipitate, which was separable into two acids by means of ether.

(1). A crude acid (about 5.3 % of the product of saponification), which was left behind after repeated extraction with ether and which, after purification by crystallisation, first from boiling water and then from alcohol, melted at $171-172^{\circ}$; determination of its neutralisation number led to the molecular weight 350.4 (sativic acid, $C_{18}H_{32}(OH)_4O_2$

= 348, melting point 173°). The results of its combustion were as follows :

0.1329 gave 0.3015 CO_2 and 0.1214 H_2O . C=61.87 ; H=10.16.

$\text{C}_{18}\text{H}_{32}(\text{OH})_4\text{O}_2$ requires C=62.07 ; H=10.34.

(2). Another crude acid (yield one-fourth of the above acid) which, on evaporating the ethereal extract to a small bulk and cooling, was obtained in a crystalline state. After recrystallisation from alcohol it melted at 126° , and had the molecular weight 317.3 (dihydroxystearic acid, $\text{C}_{18}\text{H}_{34}(\text{OH})_2\text{O}_2=316$, melting point 136°). Probably, therefore, this substance is impure dihydroxystearic acid.

No characteristic crystals of either linusic acid or isolinusic acid, $\text{C}_{18}\text{H}_{30}(\text{OH})_6\text{O}_2$, could be observed.

Neutralisation number of the solid acid.—The pure recrystallised solid acid (m.p. 43—44) from the oil was dried over sulphuric acid in an atmosphere of carbon dioxide ; a weighed quantity was dissolved in neutralised alcohol and titrated with 0.0568-normal sodium hydroxide solution, using phenolphthalein as indicator. The molecular weight found were 280.6, 277.1, and 280.9. Titrations with standard barium hydroxide solution gave the numbers 283.1 and 280.7, the mean of all the determinations being 280.5, whilst $\text{C}_{18}\text{H}_{32}\text{O}_2=280$.

Summary of the Results.

1. The principal organic acids of the oil of *Elæococca vernicia* are a solid acid, m. p. $43-44^{\circ}$, and ordinary oleic acid, the former predominating.

2. The solid acid, which Cloëz named *elæomargaric acid*, and for which Maquenne recently proposed the name *a-elæostearic acid*, has the composition $\text{C}_{18}\text{H}_{32}\text{O}_2$, and not $\text{C}_{17}\text{H}_{32}\text{O}_2$, as calculated by Cloëz, or $\text{C}_{18}\text{H}_{30}\text{O}_2$, as given by Maquenne.

3. The solid acid is, undoubtedly, a stereoisomeride of linolic acid, the bromine additive product, $C_{18}H_{32}O_4Br_2$, as well as the oxidation product, $C_{18}H_{32}(OH)_2O_4$, obtained from the former, agreeing in every respect with those obtained from the latter.

