

CCXVIII.—*Studies of Chinese Wood Oil. β -Elaeostearic Acid.*

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THE so-called elæostearic acid has been investigated by Cloëz (*Compt. rend.*, 1876, **82**, 501), Maquenne (*ibid.*, 1902, **135**, 696), Kametaka (*Trans.*, 1903, **83**, 1042), Fokin (*Zeitsch. Elektrochem.*, 1906, **12**, 759), and Majima (*Ber.*, 1909, **42**, 674; 1912, **45**, 2730). Cloëz assigned to the acid the formula $C_{17}H_{30}O_2$, and named it elæomargaric acid. Maquenne and Kametaka showed that the acid must contain eighteen carbon atoms, the former maintaining the formula $C_{18}H_{30}O_2$ from the results of careful analyses of the free acid, the latter preferring the formula $C_{18}H_{32}O_2$, since a tetrabromo-acid was obtained identical with that prepared from linolic acid. Majima obtained *n*-valeraldehyde, azelaic, and valeric acids as decomposition products of the ozonide of elæostearic acid, and found that elæostearic acid was transformed quantitatively into stearic acid by catalytic reduction. He consequently assigned the constitution $CH_3 \cdot [CH_2]_3 \cdot CH:CH \cdot [CH_2]_2 \cdot CH:CH \cdot [CH_2]_7 \cdot CO_2H$ to elæostearic acid, a conclusion also in harmony with the results described in this paper. The presence of a conjugated double linking is consistent with the tendency of wood oil to become polymerised when heated. Maquenne has shown that the action of a trace of sulphur on wood

oil or the free acid causes probably a stereoisomeric change whereby an acid (m. p. 71°) is formed, differing from elæostearic acid (m. p. 48°) in resistance to oxidation. The same acid was produced when elæostearic acid was exposed to light. Cloëz (*Bull. Soc. chim.*, 1876, [ii], **26**, 286; 1877, [ii], **28**, 24) states that wood oil when exposed to light gives an isomeric glyceride (m. p. 32°).

The results of a further investigation of the glyceride produced when Chinese wood oil is exposed to light confirm many of the statements of previous investigators.

β -Elæostearic acid (m. p. 72°) and its glyceride (m. p. 48°) are stereoisomerides of elæostearic acid (m. p. 48°) and its liquid glyceride. With the exception of the potassium salt, the derivatives of the acid absorb oxygen with rapidity, and in several cases it was impossible to prevent oxidation before analysis.

The yield of the tetrabromo-acid (m. p. 115°) is very small, and the main product of the bromination is an oily tetrabromide.

The investigation of the properties of β -elæostearic acid (m. p. 72°) has shown that it is possible to obtain definite salts characterised by great insolubility in water. The ethyl ester can be distilled under diminished pressure, and undoubtedly contains only two double linkings. The low values of the hydrogen in Maquenne's analyses must be ascribed to unavoidable oxidation during the manipulation of the acid and of its derivatives.

The study of a crystalline glyceride of a drying oil may help to throw light on the changes which occur when a drying oil is exposed to air. Some interesting results have been obtained which tend to confirm the view that polymerisation occurs during the drying of an oil.

Further investigation is in progress, and the results will be communicated in a subsequent paper.

EXPERIMENTAL.

Hankow Chinese wood oil was exposed to light in glass bottles fitted with air-tight stoppers. In a few days, depending on the season, crystals appeared, and in a year about 6 per cent. of the oil was transformed into a crystalline modification. In the dark the oil was unchanged. After treatment with acetone the crystals were collected, and washed with the solvent to remove the last traces of oil.

The solid was dried in a vacuum, and melted at 61 — 62° . The oil in the filtrate after removal of the acetone by distillation in a current of carbon dioxide was again exposed to light, and in a few days yielded another crop of crystals.

By repetition of the process a very considerable proportion of the

wood oil was transformed; in fact, when the crystallisation had been started, treatment with acetone accelerated the change when the oil was exposed again to light.

The white solid is soluble in chloroform, ether, or benzene, but very sparingly so in cold alcohol (10 grams dissolve in 200 c.c. of boiling alcohol). It is readily soluble in hot glacial acetic acid, and separates out on cooling the solution. By solution in benzene and precipitation by alcohol, crystalline rosettes of rounded plates were obtained, melting at 61—62°. Recrystallisation from hot alcohol or hot glacial acetic acid gave crystals melting at the same temperature. Although every precaution was taken to prevent absorption of oxygen, the results of a number of analyses show that it is impossible to decide between the formulæ $(C_{18}H_{29}O_2)_3C_3H_5$ and $(C_{18}H_{31}O_2)_3C_3H_5$. It was found that the substance slowly gained weight, even in a vacuum desiccator, which added to the difficulty in removing the last traces of the solvent:

0.1914 gave 0.5486 CO_2 and 0.1814 H_2O . $C=78.2$; $H=10.55$.

0.1052 „ 0.3028 CO_2 „ 0.100 H_2O . $C=78.49$; $H=10.57$.

Iodine value (W_{ijs})=183. Saponification value=191.5.

0.7952 in 14.9256 benzene gave $\Delta t = -0.297^\circ$. M.W.=879.

$(C_{18}H_{31}O_2)_3C_3H_5$ requires $C=77.92$; $H=11.16$ per cent.

Iodine value=173.5. M.W.=878.

$(C_{18}H_{29}O_2)_3C_3H_5$ requires $C=78.45$; $H=10.55$ per cent. I.V.=262.

The oxidised glyceride is quite insoluble in warm glacial acetic acid, so that the purity of the crystalline modification can be confirmed by its complete solubility in that medium. The avidity with which the substance takes up oxygen makes it necessary to keep it in sealed vessels. In an ordinary glass-stoppered bottle the percentages of carbon and hydrogen had fallen in four days from 78.2 and 10.55 to 72.5 and 9.53 respectively. Ten days afterwards the substance contained 64.63 per cent. of carbon and 8.59 of hydrogen. It could now be heated to 230° without melting, and with only a slight change in colour.

On exposure to air a decided odour of valeraldehyde was noticed, and when the weight had become constant the percentages of carbon and hydrogen had fallen to 63.9 and 8.70 respectively ($[C_{18}H_{31}O_6]_3C_3H_5$ requires $C=64.0$; $H=9.15$). When treated with potassium iodide and dilute acetic acid, iodine was liberated; on boiling with water the oxidised glyceride became yellow and spongy in texture, and the aqueous extract gave a decided coloration with Schiff's reagent and a yellow colour with titanium dioxide in dilute sulphuric acid.

It is evident that the products of oxidation include an aldehyde derived from the decomposition of a peroxide.

The original crystalline substance does not give these reactions. On exposure to air at the ordinary temperature the glyceride gained 12.15 per cent. in weight with loss of crystalline form, but without appreciable change in colour. The saponification value had risen to 412.9, and the iodine and acid values were 41.45 and 47.7 respectively.

When dry oxygen was passed over the crystalline glyceride, there was a steady increase in weight to 23 per cent., accompanied by the liberation of substances of an aldehydic and acidic nature, which were absorbed by alkali and ammoniacal silver nitrate.

When the temperature was raised to 100° and a current of dry oxygen or nitrogen was passed over the substance, there was an immediate change in colour, accompanied by a loss in weight to a constant value of 8 per cent., whilst the total gain in weight of the absorption tubes was 35 per cent. of the original weight of the substance. The final product reduced Fehling's solution, was readily soluble in alkalis, but it gave no reaction for a peroxide, and its iodine value had fallen to 38.35. Olsen and Ratner (*Eighth Int. Cong. Appl. Chem.*, 1912, Sect. Ve, Orig. Comm. 12, 165—173) have investigated the decomposition of linseed oil during drying under similar conditions.

Potassium β -Elaeostearate.—Saponification of the glyceride by alcoholic potassium hydroxide gives a crystalline potassium salt, insoluble in cold alcohol, but crystallising from hot alcoholic solution in long, rhombic plates (one part of the salt dissolves in 20 parts of boiling alcohol):

0.5666 gave 0.1566 K_2SO_4 . $K=12.39$.

0.4946 „ 0.1352 K_2SO_4 . $K=12.26$.

$C_{18}H_{31}O_2K$ requires $K=12.36$ per cent.

The salt is partly hydrolysed when warmed in aqueous solution. An analysis of the salt recrystallised from hot water gave:

0.4122 gave 0.0530 K_2SO_4 . $K=5.76$.

$C_{18}H_{32}O_2, C_{18}H_{31}O_2K$ requires $K=6.24$ per cent.

A solubility determination in water at 16.7° showed that 0.279 parts were present in 100 parts of solution.

The salt can be heated above 230° without change in colour. After recrystallisation from hot water the salt softens at 121° and melts to a jelly at 185°.

Its solubility in water is so small that it is impossible to transform it completely into the corresponding acid by the action of dilute acid in the presence of ether. The salt can be heated at 110° for an hour without change in weight, and on exposure to air at the ordinary temperature for fourteen days it gains only 5 per

cent., and in twenty-one days the total gain is 5.5 per cent.; the salt becomes yellow, and acquires a greasy surface. With Schiff's reagent the crystals become purple, pure potassium iodide and dilute acetic acid liberate iodine, but on warming with dilute sulphuric acid, filtering, and testing with titanous acid no yellow coloration ensues.

It is evident that a peroxide is formed on exposure to air, which can be decomposed to give an aldehyde but no hydrogen peroxide.

β -Elaeostearic Acid.—Twenty grams of the potassium salt were dissolved in 600 c.c. of boiling water, and excess of dilute sulphuric acid was added; the acid separated out either as an oil or as a white, crystalline solid. In order to free it from any potassium salt it was dissolved in ether, and the ether distilled off in a current of carbon dioxide. The acid was recrystallised from warm alcohol or acetone, and separated from the former in tufts of needles, but from the latter solvent in laminae with serrated edges. The melting point was 72° , which was constant after the first recrystallisation. There was no evidence of the presence of the modification of lower melting point:

0.1810 gave 0.5146 CO_2 and 0.1729 H_2O . $\text{C}=77.5$; $\text{H}=10.6$.

0.1072 „ 9.3046 CO_2 „ 0.1056 H_2O . $\text{C}=77.47$; $\text{H}=10.94$.

Iodine value (Wijs) = 175.4; 180.7; 183.5.

M.W. (Landsberger) = 283 and 306.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ requires $\text{C}=77.4$; $\text{H}=11.46$ per cent. Iodine value = 181.4. M.W. = 280.

$\text{C}_{18}\text{H}_{30}\text{O}_2$ requires $\text{C}=77.13$; $\text{H}=10.7$ per cent.

It is not possible to decide between the two formulæ from an elementary analysis, because the same difficulties were experienced as in the case of the glyceride. Although the acid is easily soluble in warm glacial acetic acid, its solubility in the cold solvent is too small to allow of a determination of the lowering of the freezing point.

Ammonium β -Elaeostearate.—Five grams of the acid, recrystallised from alcohol, were dissolved in 100 c.c. of hot alcohol, and treated with excess of alcoholic ammonia. The ammonium salt separated from the solution in lustrous lamellæ; the yield of the pure salt was 4 grams:

2.1548 gave 0.0125 NH_3 . $\text{NH}_4=5.79$.

$\text{C}_{18}\text{H}_{31}\text{O}_2\text{NH}_4$ requires $\text{NH}_4=5.71$ per cent.

The ammonium salt dissolves readily in warm alcohol or hot water, but hydrolysis occurs as in the case of potassium salt. It is insoluble in ether or cold water (100 parts of the aqueous solution contain 0.0443 parts of the salt).

Silver β -Elaostearate.—A solution of silver nitrate was added to an alcoholic solution of the ammonium salt, and the white precipitate was washed with alcohol and ether and dried in a vacuum:

0.4999 gave 0.1389 Ag. Ag=27.82.

$C_{18}H_{31}O_2Ag$ requires Ag=27.9 per cent.

Calcium β -Elaostearate.—A solution of calcium chloride was added to an alcoholic solution of the ammonium salt, and the white precipitate was washed with water until free from chlorides, and dried in a vacuum:

0.5162 gave 0.1208 $CaSO_4$. Ca=6.88.

$(C_{18}H_{31}O_2)_2Ca$ requires Ca=6.67 per cent.

Barium β -Elaostearate.—The salt was prepared in the same way as the calcium salt; it was precipitated as a white, crystalline, granular substance, and dried in a vacuum:

0.5146 gave 0.174 $BaSO_4$. Ba=10.89.

$(C_{18}H_{31}O_2)_2Ba$ requires Ba=19.82 per cent.

Ethyl β -Elaostearate.—The ethyl ester was obtained from the acid by the action of sulphuric acid and alcohol. Care must be taken to avoid excess of sulphuric acid, otherwise considerable darkening occurs during the reaction. The ethyl ester was obtained as a pale yellow oil, which absorbed oxygen so rapidly that it was difficult to remove the last traces of ether without the occurrence of oxidation. The preparation of the ester was performed in an atmosphere of carbon dioxide, and every precaution was taken to exclude oxygen:

0.1813 gave 0.5142 CO_2 and 0.1799 H_2O . C=77.35; H=11.02.

Iodine value=150.4.

$C_{20}H_{36}O_2$ requires C=77.9; H=11.66 per cent.

Iodine value=165.

The ethyl ester boiled at $232^\circ/14$ mm. without decomposition, although a considerable amount of a non-volatile oil (iodine value=94) was left, if air were allowed to pass into the flask during the distillation. An analysis of the distillate gave the following results:

0.1888 gave 0.5443 CO_2 and 0.1884 H_2O . C=77.18; H=11.98.

Iodine value=153—154.

0.8910 (in 12.7862 acetic acid) gave $\Delta t = -0.765$. M.W.=355.6.

$C_{20}H_{36}O_2$ requires M.W.=308.

Although carbon dioxide was passed into the flask during the distillation a slight oxidation of the ethyl ester occurred. Thionyl chloride could not be used for the preparation of the ester because a black, viscid mass was produced during the removal of the chloride.

On exposure to air at the ordinary temperature, ethyl β -elæostearate gained 10.24 per cent. in weight in twenty-four hours. The maximum increase was 12 per cent., which was followed by a loss in weight until a constant gain of 11.1 per cent. was obtained:

$C_{20}H_{36}O_2 + 2O$ requires gain = 10.39 per cent.

The oxidised oil reduced Fehling's solution slightly, and on treatment with Schiff's reagent became purple. When warmed with pure potassium iodide solution no iodine was liberated except on addition of a few drops of dilute sulphuric acid. The ester did not set, and remained clear; there was no matt surface, as in the case of Chinese wood oil.

Action of Bromine on β -Elæostearic Acid.

β -Elæostearic acid (1 mol.), twice recrystallised from alcohol, was dissolved in five times its weight of glacial acetic acid, and after cooling to 0° bromine (4 atoms) was added slowly until a permanent coloration ensued. The solution, which fumed very slightly, was concentrated in a vacuum at 50° , until the acetic acid was removed. A pasty solid was left, which was freed from syrup by light petroleum. The yield was 20 per cent. of the acid taken. It was recrystallised several times from alcohol, and on cooling, bunches of fine needles were obtained, melting at 115° :

0.2073 gave 0.2728 CO_2 and H_2O . $C = 35.89$; $H = 5.0$.

0.2404 „ 0.3022 AgBr. $Br = 53.4$.

$C_{18}H_{32}O_2Br_4$ requires $C = 36.0$; $H = 5.33$; $Br = 53.3$ per cent.

The tetrabromo-acid is very soluble in benzene or carbon tetrachloride, and can be recrystallised from ethyl acetate or methyl alcohol. Bromination of β -elæostearic acid in light petroleum solution gave a 33 per cent. yield of crude tetrabromo-acid, but the product was contaminated with a syrupy substance, which reduced the yield of the pure crystallised acid.

An analysis of the uncrystallisable syrup gave the following numbers:

0.2528 gave 0.3156 AgBr. $Br = 52.8$.

$C_{18}H_{32}O_2Br_4$ requires $Br = 53.3$ per cent.

Both the crystalline and syrupy tetrabromo-acids are saturated, because treatment with iodine trichloride in the form of Wijs' solution showed no further addition of halogen.

Oxidation of β -Elæostearic Acid by Potassium Permanganate.

The oxidation of the potassium salt was performed according to the directions given by Hazura and Kametaka. Owing to the

sparing solubility of the salt a very dilute solution was used, and the total bulk of the solution was about 6 litres for 25 grams of the potassium salt. The precipitate obtained on acidifying with sulphurous acid was viscid and soluble in ether. It reduced Fehling's solution, gave a purple colour with Schiff's reagent, and liberated iodine from pure potassium iodide.

The yield of crystalline, insoluble hydroxy-acids from the oxidation of the acids of linseed oil under similar conditions was found to be 20 per cent. of the acids taken.

Concentration of the filtrate from the first precipitate gave azelaic acid contaminated with its aldehyde. It was necessary to repeat the oxidation with potassium permanganate to obtain the pure acid melting at $105-106^{\circ}$ (Found, C=57.88; H=8.43. $C_9H_{16}O_4$ requires C=57.44; H=8.43 per cent.).

The yield of azelaic acid was nearly 5 grams.

The acid filtrate contained a volatile acid, which was separated by distillation in a current of steam. It possessed the characteristic odour of *n*-valeric acid (Found, Ag in silver salt=51.44. $C_5H_9O_2Ag$ requires 51.67 per cent.).

After the removal of azelaic and valeric acids the solution was examined for tartaric and succinic acids. Hydrogen peroxide and ferrous sulphate gave no coloration, which showed the absence of tartaric acid. The pyrrole reaction for succinic acid was obtained especially in the presence of zinc dust. Neuberg (*Chem. Zentr.*, 1904, ii, 1436) states that azelaic acid gives the pyrrole reaction with zinc dust, so that the test cannot be considered as quite decisive for the presence of succinic acid derivatives.

The solution was neutralised with ammonia, and silver nitrate added; the colourless silver salt was washed with water, alcohol, and ether, and dried in a vacuum:

0.3977 gave 0.1863 Ag. Ag=46.8 per cent.

The low percentage of silver confirmed the absence of tartaric and succinic acids. The silver salt was probably a mixture of azelaic and valeric acids which would contain 50.4 and 51.4 Ag respectively.

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