299. *The Seed Oil of* Onguekoa Gore *Engler. Part I. The Position of the Hydroxyl Group in the Unsaturated Monohydroxy*-C_{18} *Acid (or Acids).*

By J. P. RILEY.

The unsaturated hydroxy-acid (or possibly, -acids) of the seed fat of *Onguekoa Gore* Engler has been shown to yield on hydrogenation 8-hydroxystearic acid,* and thus the original unsaturated acid must be a straight chain C_{18} acid bearing a hydroxyl group on its eighth carbon atom.

THE tree *Onguekoa Gore* Engler syn. *Ongokea klaineana* Pierre (also known by the native names Boleka and Isano) grows wild in Equatorial Africa. It bears soft pulpy yellow fruits about 1″ in diameter, which contain buff-coloured kernels. The latter yield on extraction 60—80% of a somewhat viscous reddish oil having a rather unpleasant smell.

Steger and van Loon (*Fette u. Seifen*, 1937, **44**, 243) isolated from the oil a highly unsaturated acid to which they assigned the formula :

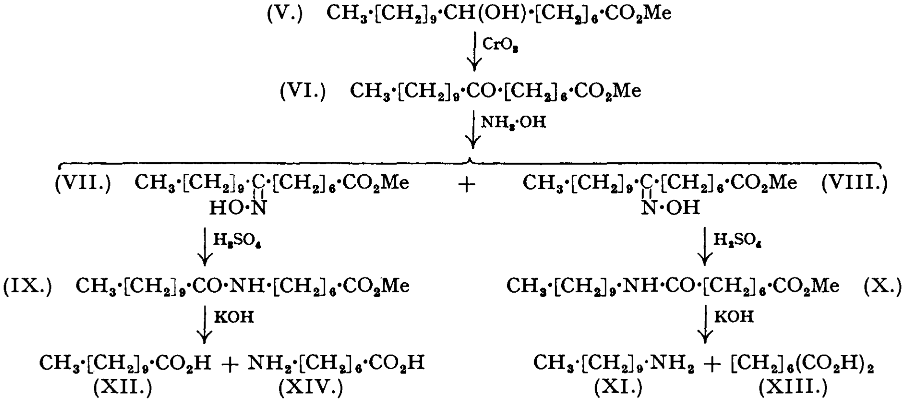
$$\text{either } \underset{\text{(I.)}}{CH_3\cdot[CH_2]_7\cdot CH{=}CH\cdot CH_2\cdot C{\equiv}C\cdot[CH_2]_4\cdot CO_2H} \text{ or } \underset{\text{(II.)}}{CH_3\cdot[CH_2]_7\cdot C{\equiv}C\cdot CH_2\cdot CH{=}CH\cdot[CH_2]_4\cdot CO_2H}$$

The same workers also prepared from the oil an acid, m. p. 38—39°, which they called isanic acid. Castille (*Annalen*, 1939, **543**, 104), who also isolated this compound and named it erythrogenic acid, was able to show that its formula was

$$\text{either } \underset{\text{(III.)}}{CH_2{=}CH{-}C{\equiv}C\cdot[CH_2]_4\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H} \text{ or } \underset{\text{(IV.)}}{CH_2{=}CH\cdot[CH_2]_4\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H}$$

These deductions were confirmed by Steger and van Loon (*Rec. Trav. chim.*, 1940, **59**, 1156) who proved that isanic acid is (IV).

From the hydrogenated mixed esters of the oil, Steger and van Loon (*loc. cit.*) obtained a hydroxy-acid, m. p. 75—78°, which they considered to be a monohydroxystearic acid not identical with 12-hydroxystearic acid, and which they later showed to be either 8- or 9-hydroxystearic acid.*



$$\text{(V.) } CH_3\cdot[CH_2]_9\cdot CH(OH)\cdot[CH_2]_6\cdot CO_2Me \xrightarrow{CrO_3} \text{(VI.) } CH_3\cdot[CH_2]_9\cdot CO\cdot[CH_2]_6\cdot CO_2Me \xrightarrow{NH_2\cdot OH}$$

$$\text{(VII.) } CH_3\cdot[CH_2]_9\cdot\underset{HO\cdot N}{\underset{\|}{C}}\cdot[CH_2]_6\cdot CO_2Me \quad + \quad CH_3\cdot[CH_2]_9\cdot\underset{N\cdot OH}{\underset{\|}{C}}\cdot[CH_2]_6\cdot CO_2Me \text{ (VIII.)}$$

$$\text{(VII.)} \xrightarrow{H_2SO_4} \text{(IX.) } CH_3\cdot[CH_2]_9\cdot CO\cdot NH\cdot[CH_2]_6\cdot CO_2Me \xrightarrow{KOH} \underset{\text{(XII.)}}{CH_3\cdot[CH_2]_9\cdot CO_2H} + \underset{\text{(XIV.)}}{NH_2\cdot[CH_2]_6\cdot CO_2H}$$

$$\text{(VIII.)} \xrightarrow{H_2SO_4} CH_3\cdot[CH_2]_9\cdot NH\cdot CO\cdot[CH_2]_6\cdot CO_2Me \text{ (X.)} \xrightarrow{KOH} \underset{\text{(XI.)}}{CH_3\cdot[CH_2]_9\cdot NH_2} + \underset{\text{(XIII.)}}{[CH_2]_6(CO_2H)_2}$$

It was with the aim of determining the position of the hydroxyl group unequivocally that the present work was carried out. A concentrate of the unsaturated hydroxy-acid was prepared by low-temperature crystallisation of the mixed acids from the oil, which were esterified with methyl alcohol and hydrogenated at 105° using Raney nickel. The hydrogenated ester was acetylated and fractionally distilled to remove saturated esters and polymerised material. The recovered acetylated esters were hydrolysed, re-esterified with methyl alcohol, and then submitted to the process first used by Baruch (*Ber.*, 1894, **27**, 127) in the elucidation of the structure of oleic acid, and more recently employed by Ross, Gebhart, and Gerecht (*J. Amer. Chem. Soc.*, 1949, **71**, 283) for the examination of peroxidised methyl oleate. The methyl hydroxystearate (V) was oxidised

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* Geneva numbering (CO_2H = 1).

with chromium trioxide to the corresponding methyl ketostearate (VI), and the latter converted into its oximes (VII and VIII). The oximes were submitted to the Beckmann rearrangement and the resulting mixture of amides (IX and X) was hydrolysed, yielding *n*-decylamine (XI), undecanoic acid (XII), and suberic acid (XIII) [the amino-acid (XIV) was not isolated]. These products indicate that the hydroxy-acid formed by hydrogenation of the unsaturated hydroxy-acid present in the oil is 8-hydroxyoctadecanoic acid.

EXPERIMENTAL.

Seeds of *Onguekoa Gore* Engler from the Cameroons were extracted first with light petroleum (b. p. 40—60°) and then with ether, giving an oil with the following characteristics :

	Petroleum-extracted oil.	Ether-extracted oil.
Yield	15·4%	45·2%
Colour	Light yellow	Dark brown
Free fatty acid (as oleic)	49·3%	36·3%
Iodine value (Wijs, 30 minutes)	205·8	198·4
Acetyl value *	—	89·3
Saturated acids (Bertram)	2·5%	1·8%
Unsaponifiable	3·2%	5·3%

* Of methyl esters of the mixed acids.

Preparation of a Concentrate of the Unsaturated Hydroxy-acid.—The ether-extracted oil (130 g.) was hydrolysed for 1 hour with boiling 10% alcoholic potassium hydroxide (650 ml.), and the unsaponifiable matter [8·28 g.; I.V. (Wijs) 290·9] was extracted with ether. The recovered acids (116·9 g.) were boiled four times with 300-ml. portions of light petroleum (b. p. 40—60°) and kept overnight at 0° before the upper layer was decanted. The petrol-insoluble acids [42·2 g.; I.V. (Toms) 177·9; $E^{1\%}_{1\,\text{cm.}}$ at 239 mμ., 96·1; at 253 mμ., 88·1; at 267 mμ., 90·8; at 283 mμ., 81·4] were esterified at room temperature with 200 ml. of methyl alcohol containing 0·5% of hydrogen chloride, yielding 40·4 g. of neutralised methyl esters [I.V. (Toms) 198·9].

Hydrogenation.—The methyl esters (20·45 g.) were hydrogenated at 105° using Raney nickel catalyst (Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471), 3·54 l. of hydrogen (at N.T.P.) being absorbed. The hydrogenated ester had I.V. (Wijs) 30·6, hence the iodine value of the original ester was 228.

Acetylation.—The hydrogenated ester (20·2 g.) was acetylated under reflux with 20 ml. of acetic anhydride for 2 hours. The excess of anhydride was destroyed by boiling with water for 1 hour. The acetylated product was extracted with ether, and acetic acid removed by washing with 10% aqueous potassium hydroxide. The acetyl compound (20·65 g.) was fractionally distilled under reduced pressure through a packed and electrically heated column to remove non-hydroxy-esters and polymerised material.

Fraction.	G.	B. p./*ca.* 0·1 mm.	Sap. equiv.	I.V.	Fraction.	G.	B. p./*ca.* 0·1 mm.	Sap. equiv.	I.V.
1	1·81	up to 132°	215·3	9·8	5	3·25	173°	173·1	—
2	2·11	132—148	288·4	7·8	6	1·41	173 falling	175·4	25·0
3	2·54	148—158	269·4	5·5	7	0·82	Column washings	183·2	—
4	2·58	160—172	206·8	—	8	5·40	Residue	224·9	65·9
					Total	19·92			

The fatty acids obtained by hydrolysis of fractions 4—7 (total, 6·71 g.) were combined and esterified with 30 ml. of methyl alcohol containing 0·5% of hydrogen chloride; the yield of methyl ester was 5·86 g.

Oxidation of Methyl Esters (V).—The methyl ester (5·86 g.) in acetic acid (60 ml.) was oxidised at room temperature with a 10% solution of chromium trioxide in acetic acid (24 ml.). The reaction was somewhat exothermic and the flask was cooled in running water. After 30 minutes at room temperature, the reaction mixture was poured into water (500 ml.), and sulphur dioxide was passed into the solution. The resultant keto-ester was extracted with ether, and the ethereal extract washed several times with water and then with 10% aqueous potassium hydroxide. The ether was removed by distillation after being washed free from alkali, yielding methyl 8-ketostearate (VI) (5·24 g.), m. p. 42·7—44·3°.

Preparation of the Oximes (VII *and* VIII) *from Methyl Ketostearate.*—Methyl 8-ketostearate (5·22 g.) in 80% alcohol (45 ml.) was treated with solutions of hydroxylamine hydrochloride (4 g.) in 80% alcohol (15 ml.) and of fused sodium acetate (6 g.) in 80% alcohol (15 ml.). The mixture was boiled under reflux for 2 hours and most of the alcohol was then distilled off. The product was poured into water, and the mixed oximes (VII and VIII) were extracted with ether. The mixed oximes (5·40 g.) consisted of a light yellow oil which did not solidify at −10°.

Beckmann Rearrangement.—The mixture of oximes (5·40 g.) was heated with concentrated sulphuric acid (30 ml.) at 100° for 1 hour. The product, when cool, was poured on ice (100 g.), and the mixed amides (IX and X) (5·21 g.) were separated by filtration, washed with water till free from acid, and dried *in vacuo*.

Hydrolysis of the Amides (IX *and* X).—The mixed amides (5·11 g.) were heated in a steel bomb at 170° for 3 hours with 30% potassium hydroxide solution (20 ml.). After cooling, the bomb was opened and the aqueous liquid was acidified with sulphuric acid and steam-distilled, 2 l. of distillate being collected and retained for extraction of the steam-volatile acid (XII). The residue from the steam-distillation was extracted with ether, when 1·31 g. of a mixture of dibasic acid (XIII), unhydrolysed amide, and saturated acid (?) were obtained. The aqueous residue from the extraction was made alkaline with sodium hydroxide solution and steam-distilled; 1·5 l. of distillate were collected and gave, on extraction with ether, 1·58 g. of volatile amine (XI) which was purified by distillation under reduced pressure (b. p. 108°/12 mm.). The amino-acid (XIV) in the aqueous residue from the steam-distillation was not recovered.

(a) *Steam-volatile acid* (XII). The distillate (2 l.) obtained from the acidic solution was extracted with ether, and 0·852 g. of undecanoic acid was recovered (Found: S.E., 187·0. Calc. for $C_{11}H_{21}·CO_2Me$: S.E., 186·0); the *p*-bromophenacyl ester had m. p. 67—68° alone or mixed with authentic *p*-bromophenacyl undecanoate (m. p. 67—68°).

(b) *Dibasic acid* (XIII). The brownish solid (1·31 g.) extracted with ether from the acidic steam-distillation residue was boiled with three 200-ml. portions of water, and the aqueous extracts were filtered hot through a fine filter paper to remove an insoluble dark oil (0·708 g.) which was rejected. The combined aqueous solutions were evaporated to 20 ml. and cooled to room temperature, the precipitated dibasic acid (0·377 g.; m. p. 126—131°) was filtered off and recrystallised twice from 20 ml. of water at 0° and twice from 15 ml. of ethyl acetate at 0°, yielding 0·105 g. of dibasic acid [Found: S.E., 87·3. Calc. for $C_6H_{12}(CO_2H)_2$: S.E., 87·0), m. p. 138·5—140·3° alone or mixed with suberic acid (m. p. 139—141°).

(c) *Steam-volatile amine* (XI). The distilled amine (0·256 g.) in ligroin (b. p. 80—100°) (10 ml.) was treated with a solution of α-naphthyl *iso*cyanate (0·30 g.) in ligroin (b. p. 80—100°) (10 ml.). The resultant gelatinous solid was filtered off, pressed, washed with light petroleum (b. p. 40—60°), and dried *in vacuo*. The crude product (0·127 g.) was recrystallised from ligroin and yielded *N*-*n*-decyl-*N'*-α-naphthylurea, m. p. 128—129° alone or mixed m. p. with an authentic specimen (m. p. 128—129°).

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