

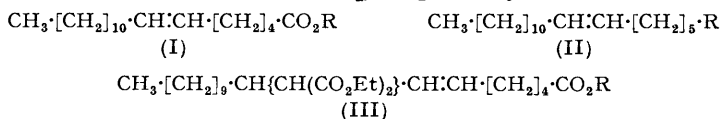
**913. The Seed Fat of *Myrrhis odorata*. Contributions to the Chemistry of Petroselinic Acid.**

By G. R. CLEMO and R. STEVENS.

The seeds of *Myrrhis odorata* yield the glyceride of petroselinic acid, an extension of whose chemistry is described.

PETROSELINIC ACID (*cis*-octadec-6-enoic acid) \* (I; R = H) was first isolated from parsley seed oil (Vongerichten and Kohler, *Ber.*, 1909, **42**, 1638; cf. Hilditch, "The Constitution of the Natural Fats," 2nd. Edn., Chapman and Hall Ltd., London, 1949, p. 179).

We have now characterised this acid in the seed fat of *Myrrhis odorata* (Sweet Cicely), the air-dried seeds of which contain 13—17% of oil which after molecular distillation consists almost entirely of glycerol tripetroselinate whose properties agree with those recorded by Vongerichten and Kohler (*loc. cit.*). Hydrolysis of the glyceride gave petroselinic acid (I; R = H), characterised by reduction to stearic acid, ozonolysis to lauric and adipic acid, and by the preparation of several derivatives. The methyl ester and amide were reduced with lithium aluminium hydride to octadec-6-enyl alcohol (II; R = OH) and the amine (II; R = NH<sub>2</sub>), respectively.



Experiments to demonstrate the geometrical configuration of the acid (assumed to be *cis* by analogy with oleic acid), by the semihydrogenation of tariric acid (octadec-6-ynoic acid) were in progress when Lumb and J. C. Smith (*Chem. and Ind.*, 1952, 358) announced the synthesis of tariric and petroselinic acid.

With methyl petroselinate and *N*-bromosuccinimide an oily monobromo-compound was obtained which decomposed on attempted distillation. Dehydrobromination by collidine gave a product shown by ozonolysis and unsaturation to be octadeca-6: 8-dienoic acid. This showed an absorption maximum in the ultra-violet at 232 m $\mu$  (log  $\epsilon$  = 4.27) in agreement with the absorption of the isomeric 9: 11-dienoic acid, recorded by Hulst (*Rec. Trav. chim.*, 1935, **54**, 639, 644).

The bromo-compound was therefore chiefly methyl 8-bromopetroselinate. The bromine atom was replaced by hydroxyl but attempts to replace it by the cyano-group failed. With sodiomalonic ester the bromo-ester gave (III; R = Me), which was hydrolysed and decarboxylated to the corresponding dibasic acid; no success has been achieved in Dieckmann cyclisations of its methyl ester.

#### EXPERIMENTAL

Microhydrogenations were performed in ethanol, Adams's platinum catalyst being used.

*Isolation of Glyceride and Acid.*—The air-dried seeds (25 g.) were extracted overnight with ether in a Soxhlet apparatus, and the extract distilled from a bath at 150—160°/4 × 10<sup>-4</sup> mm., giving an oil (3.0 g.) which solidified on cooling; m. p. 29—30° (Vongerichten and Kohler, *loc. cit.*, give m. p. 32°) (Found : C, 77.0; H, 12.4. Calc. for C<sub>57</sub>H<sub>104</sub>O<sub>6</sub> : C, 77.4; H, 11.8%). Catalytic hydrogenation gave tristearin, m. p. 68—70° (lit. 71°).

The crude undistilled glyceride on saponification for 3 hours with boiling 2*N*-methanolic potassium hydroxide gave the acid, b. p. 148—152°/0.15 mm., *n*<sub>D</sub><sup>25</sup> 1.4565, m. p. 29—30° (Found : C, 76.4; H, 12.2. Calc. for C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> : C, 76.6; H, 12.0%); *p*-bromophenacyl derivative, plates (from ethanol), m. p. 44—45° (Found : C, 65.6; H, 8.6. C<sub>26</sub>H<sub>39</sub>O<sub>3</sub>Br requires C, 65.2; H, 8.15%). Catalytic hydrogenation gave stearic acid, m. p. 70—71°. 6: 7-Dihydroxystearic acid, prepared by the oxidation of the acid with peracetic acid, had m. p. 114—115° (Hilditch and Jones, *J. Soc. Chem. Ind.*, 1927, **46**, 126*r*, record m. p. 114—115°) (Found : C, 68.7; H, 11.6. Calc. for C<sub>18</sub>H<sub>34</sub>O<sub>4</sub> : C, 68.4; H, 11.4%).

*Ozonolysis of the Acid.*—The acid (1.5 g.) in light petroleum was ozonised at 0° and the ozonide decomposed by refluxing for 6 hr. with sodium hydrogen sulphite solution saturated

\* Geneva nomenclature, CO<sub>2</sub>H = 1, is used throughout.

with sulphur dioxide. An ethereal extract of the resulting solution gave a white solid, which after being washed with ether had m. p. 147—148°, alone or admixed with adipic acid. The ether washings gave lauric acid, m. p. 44° (lit. 44°).

*Reduction of Methyl Petroselinate*.—The ester (2.3 g.) in dry ether (30 ml.) was added dropwise to excess of lithium aluminium hydride in ether (20 ml.). After 30 minutes the excess of reagent was decomposed with acetone, and the solution made alkaline (2*N*-sodium hydroxide) and extracted with ether, from which extract there was obtained *octadec-6-en-1-ol* (1.4 g.), b. p. 142—143°/0.5 mm.,  $n_D^{19}$  1.4642 (Found: C, 80.7; H, 13.4.  $C_{18}H_{36}O$  requires C, 80.6; H, 13.7%). Microhydrogenation showed 1.0 $\bar{f}$  and gave a product, m. p. 55—56° (Meyer and Reid, *J. Amer. Chem. Soc.*, 1933, **55**, 1374, record m. p. 57—58° for octadecan-1-ol).

*Petroselinoyl Chloride*.—The acid (2.6 g.) and redistilled thionyl chloride were kept overnight, the excess of reagent then removed, and the acid *chloride* distilled, as a pale yellow oil, b. p. 144—146°/2.0 mm. (Found: C, 71.5; H, 10.9.  $C_{18}H_{33}OCl$  requires C, 71.9; H, 11.0%). The amide (from light petroleum) had m. p. 74—75° (Vongerichten and Kohler, *loc. cit.*, report m. p. 76°) (Found: C, 76.6; H, 12.95; N, 5.1. Calc. for  $C_{18}H_{35}ON$ : C, 76.9; H, 12.5; N, 5.0%); the *anilide* (from aqueous alcohol) had m. p. 62—63° (Found: C, 80.3; H, 11.2; N, 4.3.  $C_{24}H_{39}ON$  requires C, 80.7; H, 10.9; N, 3.9%).

*Octadec-6-enylamine* (II; R = NH<sub>2</sub>).—The amide (400 mg.) was refluxed with lithium aluminium hydride (250 mg.) in tetrahydrofuran (25 ml.) for 30 minutes, giving the *base* (200 mg.), b. p. 113—116°/0.5 mm., m. p. 18—20° (this rose after several weeks to 40—45°) (Found: C, 80.8; H, 14.1; N, 4.9.  $C_{18}H_{37}N$  requires C, 80.9; H, 13.9; N, 5.2%). Microhydrogenation showed 1.0 $\bar{f}$  and gave octadecan-ylamine, m. p. 46°.

*Reaction of N-Eromosuccinimide with Methyl Petroselinate*.—The ester (2.0 g.), *N*-bromosuccinimide (1.45 g.), and dibenzoyl peroxide (50 mg.) were refluxed in carbon tetrachloride (25 ml.) for 2 hours. Succinimide (0.75 g.) was removed and the crude bromo-compound (Found: Br, 20.8. Calc. for  $C_{19}H_{35}O_2Br$ : Br, 21.3%) refluxed with collidine (10 ml.). After cooling, dilution with ether, and removal of collidine hydrobromide (1.3 g.), the ethereal solution washed with water, dilute hydrochloric acid, and sodium carbonate solution and distilled, giving methyl octadeca-6:8-dienoate (1 g.), b. p. 154—156°/0.1 mm. (Found: C, 77.2; H, 11.9.  $C_{19}H_{34}O_2$  requires C, 77.6; H, 11.6%). Light absorption: Maximum in EtOH, 232  $\mu$  ( $\log \epsilon$  4.27) [Hulst, *loc. cit.*, records  $\lambda_{max}$  231  $\mu$  ( $\log \epsilon$  4.55) for the isomeric 9:11-dienoic acid]. Hydrolysis gave *octadeca-6:8-dienoic acid*, b. p. 153—155°/0.1 mm. (Found: C, 76.9; H, 11.8.  $C_{19}H_{34}O_2$  requires C, 77.1; H, 11.4%). The *p*-bromophenacyl derivative had m. p. 79—81° (from ethanol) (Found: C, 64.9; H, 8.0.  $C_{26}H_{37}O_3Br$  requires C, 65.4; H, 7.8%). Microhydrogenation showed 2.0 $\bar{f}$  and gave stearic acid, m. p. 70—71°.

*Ozonolysis of Octadeca-6:8-dienoic Acid*.—The acid (1.8 g.) was ozonised in glacial acetic acid (30 ml.), and the mixture then refluxed with 100-vol. hydrogen peroxide for three hours and steam-distilled, giving decanoic acid (400 mg.) (Found: C, 69.7; H, 11.9%; equiv., 173. Calc. for  $C_{10}H_{20}O_2$ : C, 69.8; H, 11.6%; equiv., 172). The *p*-bromophenacyl ester had m. p. 62—64°, alone or admixed with *p*-bromophenacyl decanoate.

The residue from the steam-distillation was extracted with ether and then in a continuous extractor, the extract was methylated with diazomethane, and the methyl ester (300 mg.), b. p. 120—121°/25 mm., hydrolysed, giving adipic acid, m. p. 147—148° (after sublimation).

*8-Hydroxypetroselinic Acid*.—Methyl 8-bromopetroselinate (3.6 g.) in methanol (25 ml.) was shaken overnight with moist silver oxide (from silver nitrate: 4.0 g.) and filtered, the residue washed with methanol, and the combined filtrates distilled, giving *methyl 8-hydroxypetroselinate* (1.4 g.), b. p. 132—134°/0.2 mm. (Found: C, 73.4; H, 11.8%;  $\bar{f}$ , 1.  $C_{19}H_{36}O_3$  requires C, 73.1; H, 11.5%). The *acid* had b. p. 160—161°/0.5 mm. (Found: C, 72.05; H, 11.4.  $C_{18}H_{34}O_3$  requires C, 72.5; H, 11.4%).

*Reaction of Methyl 8-Bromopetroselinate with Sodiomalonic Ester*.—Methyl 8-bromopetroselinate (from 4.3 g. of ester) was refluxed with ethyl sodiomalonate (from 0.35 g. of sodium) in benzene (25 ml.) for 48 hours. The fraction of b. p. 190—191°/0.5 mm. (1.5 g.) (Found: C, 69.15; H, 10.02;  $\bar{f}$ , 1.0. Calc. for  $C_{26}H_{46}O_6$ : C, 68.7; H, 10.1%), on hydrolysis and distillation gave the dibasic acid (0.7 g.) from which the dimethyl ester, b. p. 157°/0.2 mm., was prepared. Both this ester and its *dihydro*-derivative (Found: C, 71.5; H, 11.5.  $C_{22}H_{42}O_4$  requires C, 71.4; H, 11.4%) failed to cyclise under Dieckmann conditions.

The authors thank Thomas Hedley and Co. Ltd. for financial help to one of them (R. S.).