

# PETROSELINIC ACID: OCCURRENCE IN SOME UMBELLIFERÆ SEED FATS

BY K. N. MENON, F.A.SC. AND P. S. RAMAN

(Maharaja's College, Ernakulam and Madras University Laboratory, Guindy)

Received September 13, 1952

THE umbelliferæ seed fats are characterised by the presence of  $\Delta^6$ -octadecenoic acid or petroselinic acid as the chief component fatty acid. Its lead salt is sparingly soluble in cold alcohol, by reason of which it is separated from oleic and linoleic acids, the other unsaturated acids usually present in these fats.

The present investigation deals with the examination of seed fats derived from three typical members of the umbelliferæ, much grown in India, viz., *Cuminum cyminum* (Cumin), *Anethum sowa* (Dill) and *Ptychotis Ajowan* (Ajowan). Grimme,<sup>1</sup> who isolated these fats, reports only on some of the constants. A detailed analysis of the fatty acids has shown that petroselinic acid is present to the extent of 21, 45 and 42% respectively of the total fatty acids in these three seed fats. Cumin seed fat is exceptional by the presence of stearic and arachidic acids, in addition to palmitic acid, the only saturated acid usually present in umbelliferæ seed fats.

The identity of petroselinic acid was proved by first obtaining 6:7-dihydroxy stearic acid by alkaline permanganate oxidation and then oxidising the dihydroxy acid with lead tetracetate yielding adipic semialdehyde, lauric aldehyde and the corresponding acids. Oxidation with peracetic and performic acids gave the lower melting dihydroxy-acid of m.p. 117°. The *trans*-acid, formed from the *cis*-acid with nitrous acid gave, on the other hand, the higher melting dihydroxy acid of m.p. 122°. Instead of the usual hydrogen peroxide-organic acid mixture, a modified procedure involving a mixture of barium peroxide-sulphuric acid-organic acid, was employed with good results. These oxidation products are exactly the reverse of those obtained by alkaline permanganate oxidations, wherein the *cis*-acid gives a product melting at 122° and the *trans*-acid a product melting at 117°. These results involving an inversion with alkaline permanganate are in full agreement with the known observations in the case of two other well-known *cis-trans* systems, viz., oleic-elaidic and erucic-brassicidic.

## EXPERIMENTAL

I. The oil, in each case, was obtained by extraction of the seeds with benzene, steam distillation to remove the volatile portion and final purification with dilute carbonate solution. The fatty acids, obtained as usual,

were separated into solid and liquid portions by lead salt separation, most of the non-saponifiable matter in the case of cumin and dill being removed before working up the soap for acids. The constants of the oil, the solid and liquid acids are:—

		Cumin	Dill	Ajowan
Pure oil	{ Sap. value	183.4	173.4	189.3
	{ Iod. value	94.34	93.54	101.3
	{ N. S. matter	9.5	8.6	2.9
Solid acids	{ p.c. of total acids	30.2	50.9	43.1
	{ Acid value	197.7	201.9	198.9
	{ Iod. value	59.92	76.63	84.16
Liquid acids	{ p.c. of total acids	69.8	49.1	56.9
	{ Acid value	193.5	190.5	186.8
	{ Iod. value	118.4	110.9	124.6

Note.—1. I. V. determinations by Hanus method.

2. The liquid acids still contained small quantities of non-saponifiable matter.

II. The fatty acid composition was determined by ester fractionation.

Cumin .. Palmitic 3.4%, stearic 3.3%, arachidic 4.9%, petroselinic 21.3%, oleic 39.3% and linoleic 27.9% by weight.

Dill .. Myristic 0.6%, palmitic 6.7%, stearic traces only, petroselinic 44.8%, oleic 34.4% and linoleic 13.3% by weight.

Ajowan .. Palmitic 2.6%, petroselinic 41.8%, oleic 34.8% and linoleic 20.7% by weight.

Petroselinic acid<sup>2</sup> was confirmed in each case by saponifying its ester and oxidising the liberated acid with alkaline permanganate. The different samples of the dihydroxy acid (m.p. 122°) obtained from the three different fats, were mixed with one other and the m.p. in each case showed no depression. Oleic and linoleic acids were confirmed by means of their hydroxy derivatives.

III. *Tetracetate oxidation of 6:7-dihydroxy stearic acid.*—1.6 gm. of the hydroxy acid were suspended in dry benzene (30 c.c.), 2 gm. of lead tetracetate added and the mixture shaken on a mechanical shaker. After about 15 minutes almost the whole of the solid disappeared and afterwards a white solid began to separate. At the end of 45 minutes the benzene solution was filtered from the insoluble matter, the residue washed with benzene and the washings added to the original filtrate. The residue after removing benzene which was previously washed with water, was treated with excess of semicarbazide hydrochloride-sodium acetate in dilute alcohol, heated

on the water-bath for 2 hours, cooled and diluted. The precipitate was collected, shaken with light petrol and filtered. The product, crystallised from dilute alcohol, had a melting point of  $102^{\circ}$ , the melting point of lauric aldehyde being<sup>2</sup>  $100-1^{\circ}$ . The petroleum-ether solution yielded a small quantity of lauric acid, m.p.  $43^{\circ}$ .

The aqueous washings of the benzene solution were concentrated to a small bulk and treated with a concentrated solution of semicarbazide hydrochloride-sodium acetate. After heating on the water-bath for a short time, the solution was cooled and the solid collected. It crystallised from water in colourless plates, m.p.  $178-79^{\circ}$  and was soluble in bicarbonate solution. Analysis proved it to be adipic semialdehyde semicarbazone (Found C, 45.04% and H, 7.18%.  $C_7H_{13}N_3O_3$  requires 44.92 and 6.95% respectively).

The solid that separates during the oxidation is the lead salt of adipic acid. The salt was decomposed with dilute hydrochloric acid, lead chloride removed and the filtrate evaporated to dryness on the water-bath. The residue, on crystallisation from benzene, melted at  $150^{\circ}$  and showed no depression with pure adipic acid ( $149-50^{\circ}$ ).

IV. *Per-acid oxidation*.—Pure petroselinic acid was obtained from ajowan seed fatty acids and was crystallised at  $0^{\circ}$  from dilute alcohol. The acid, thus purified, showed a m.p.  $28-29^{\circ}$  and an I.V. 88.5 (theory 90). Petroselaidic acid was prepared as follows: To one gm. of Poutet's reagent, cooled by ice water, was added 12 gm. of pure petroselinic acid and the mixture stirred well. After maintaining the mixture at  $10^{\circ}$  for half-an-hour, it was left overnight at the room temperature. The resulting solid mass was ground well with water, filtered, washed free of mineral acid and dried at the pump. It was dissolved in a small volume of hot dilute alcohol and allowed to cool slowly. The separated solid was collected, spread on a filter-paper and pressed well to remove adhering petroselinic acid. The crystallisation was repeated until an almost pure product of m.p.  $50-52^{\circ}$  was obtained. On oxidation with alkaline permanganate at  $20-23^{\circ}$  a dihydroxy acid melting at  $115-17^{\circ}$  was obtained.

To a mixture of 0.5 c.c. of concentrated sulphuric acid and 0.4 c.c. of water, cooled by ice-salt mixture, was added 1.5 gm. of 80% barium peroxide in 3 portions. The cold paste was added to a suspension of 1.8 gm. of petroselinic acid in 25 c.c. of 90% formic acid cooled by ice water. The mixture was shaken well and allowed to warm up gradually. In a few minutes the temperature rose to  $35^{\circ}$  and was maintained for 2 hours at  $38-40^{\circ}$ , by surrounding with warm water. After leaving the mixture overnight at room temperature, it was poured into water and extracted with

ether. The hydroxy-formoxy compound thus obtained was refluxed for 3 hours with 25 c.c. of 2N-alcoholic potash, alcohol removed and acidified with hydrochloric acid. The resulting acid, after crystallisation from alcohol, gave m.p. 115–17° and molecular weight 313 as against the theoretical value 314. The melting point was not depressed on mixing with the hydroxy acid obtained by alkaline permanganate oxidation of petroselaidic acid.

The peracetic oxidation was carried out exactly as above, using acetic acid instead of formic acid. The dihydroxy acid obtained melted at 115–17°.

Petroselaidic acid, on oxidation either with peracetic or performic acid, gave a dihydroxy acid of m.p. 122° undepressed by mixing with the dihydroxy acid obtained by alkaline permanganate oxidation of petroselinic acid.

#### SUMMARY

The naturally occurring *cis*-petroselinic acid gave the lower melting dihydroxy acid, while the *trans*-isomer gave the higher melting dihydroxy acid on per-acid oxidation.

#### REFERENCES

- |                        |   |
|------------------------|---|
| 1. Grimme              | .. <i>Pharm. Zentr.</i> , 1911, <b>52</b> , 661.        |
| 2. Hilditch and Jones  | .. <i>J. Soc. Chem. Ind.</i> , 1927, <b>46</b> , 174 T. |
| Van Loon               | .. <i>Rec. Trav. Chim.</i> , 1927, <b>46</b> , 492.     |
| Steger and van Loon    | .. <i>Ibid.</i> , 1928, <b>47</b> , 471.                |
| Tsujimoto and Koyanagi | .. <i>Bull. Chem. Soc.</i> , 1933, <b>8</b> , 161.      |