PETROSELINIC ACID: OCCURRENCE IN SOME
UMBELLIFERÆ SEED FATS

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Received September 13, 1952

The umbelliferae seed fats are characterised by the presence of $\Delta^8$-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 umbelliferae, much grown in India, viz.,
Cuminum cuminum (Cumin), Anethum sowa (Dill) and Pyschositis Ajowan
(Ajowan). Grimme, 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 umbelliferae 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 per-
formic 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 agree-
ment with the known observations in the case of two other well-known
cis-trans systems, viz., oleic-elaicid and erucic-brassicid.

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 purifica-
tion 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:

<table>
<thead>
<tr>
<th></th>
<th>Cumin</th>
<th>Dill</th>
<th>Ajowan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sap. value</td>
<td>183·4</td>
<td>173·4</td>
<td>189·3</td>
</tr>
<tr>
<td>Iod. value</td>
<td>94·34</td>
<td>93·54</td>
<td>101·3</td>
</tr>
<tr>
<td>N. S. matter</td>
<td>9·5</td>
<td>8·6</td>
<td>2·9</td>
</tr>
<tr>
<td>Solid acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p.c. of total acids</td>
<td>30·2</td>
<td>50·9</td>
<td>43·1</td>
</tr>
<tr>
<td>Acid value</td>
<td>197·7</td>
<td>201·9</td>
<td>198·9</td>
</tr>
<tr>
<td>Iod. value</td>
<td>59·92</td>
<td>76·68</td>
<td>84·10</td>
</tr>
<tr>
<td>Liquid acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p.c. of total acids</td>
<td>69·8</td>
<td>49·1</td>
<td>56·9</td>
</tr>
<tr>
<td>Acid value</td>
<td>139·5</td>
<td>190·5</td>
<td>186·8</td>
</tr>
<tr>
<td>Iod. value</td>
<td>118·4</td>
<td>110·9</td>
<td>124·6</td>
</tr>
</tbody>
</table>

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 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 depres-
sion. Oleic and linoleic acids were confirmed by means of their hydroxy
derivatives.

III. Tetracete 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 tetra-
cetate 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°, the melting point of lauric aldehyde being 100–1°. The petroleum-ether solution yielded a small quantity of lauric acid, m.p. 43°.

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° and was soluble in bicarbonate solution. Analysis proved it to be adipic semialdehyde semicarbazone (Found C, 45·04% and H, 7·18%. $C_{7}H_{13}N_{8}O_{3}$ 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° and showed no depression with pure adipic acid (149–50°).

IV. _Per-acid oxidation._—Pure petroselinic acid was obtained from ajowan seed fatty acids and was crystallised at 0° from dilute alcohol. The acid, thus purified, showed a m.p. 28–29° 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° 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° was obtained. On oxidation with alkaline permanganate at 20–23° a dihydroxy acid melting at 115–17° 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° and was maintained for 2 hours at 38–40°, 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.

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