XLIII. SEED FATS OF THE *UMBELLIFERAE*.

I. *HERACLEUM SPHONDYLIIUM* AND *ANGELICA SYLVESTRIS*.

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In 1909 Vongerichten and Kohler [1909] established the presence of an isomeric solid oleic acid, petroselinic acid, in the fatty oil of parsley seeds (*Petroselinum sativum*). In a recent analysis of the mixed fatty acids of this oil [1927] we found 76 % of petroselinic ($\Delta^{6:7}$ -octadecenoic), 15 % of oleic, 5.5 % of linoleic, 2.5 % of palmitic and 1 % of higher saturated acids.

Scherer [1909] observed a solid oleic acid (presumably petroselinic acid) in the seed fats of two other Umbellates, *Pimpinella anisum* and *Foeniculum capillaceum*, and Palazzo and Tamburello [1914] have stated that the same acid is present in the fatty oil of *Hedera helix* seeds (Araliaceae). We have commenced the examination of a number of umbelliferous seed fats in order to ascertain whether this acid is invariably present therein, and how its relative proportion compares with that of the co-existent oleic ($\Delta^{9:10}$ -octadecenoic) acid.

In this communication we deal with two common wild species of the Order, the seeds of which were collected in the early autumn of 1926 in the Wirral peninsula, Cheshire. The fruits were collected in dry weather, only those umbels which shed their fruits when knocked being chosen. The collected fruits were dried for some weeks in thin layers which were frequently turned, and were then shaken first in a coarse sieve to remove the small ray stalks, and then in a very fine sieve to remove any adhering dust. Due care was taken, by comparison with specimens in the Hartley botanical laboratories of this University, to ensure the respective identity of the two species, namely, *Heracleum sphondylium* (Cow parsnip or Hogweed) and *Angelica sylvestris* (Wild angelica).

In both cases the fruits, like those of many Umbellates, are characterised by relatively large winged ribbed carpels (mericarps), which contain notable amounts of fat in the vittae or oil ducts; it was, of course, not feasible to separate the seed proper from the rest of the fruit and therefore the fats examined consist of a mixture of the seed and carpel oils.

The seeds of the *Umbelliferae*, again, contain in general an unusually large proportion of non-fatty matter of various kinds which is extracted under the same conditions as the fat, and this adds to the complexity of the investigation.

In the case of *Heracleum* the non-fatty compounds present are mainly esters of lower fatty acids and alcohols, *e.g.* octyl acetate [Zincke, 1869; Möslinger, 1877], whilst *Angelica* seeds contain esters of valeric and other acids [Müller, 1881]. Precautions were taken to exclude these compounds as far as possible before the fatty acid mixtures were examined in detail.

The dried seeds were ground and extracted in a Soxhlet apparatus with ether; the recovered oil was in each case dark coloured, possessed a strong odour of lower fatty acids, and contained an appreciable amount of resinous matter. The yields and characteristics of the products obtained were as follows:

	<i>Heracleum sphondylium</i>	<i>Angelica sylvestris</i>
Dry seed taken (g.)	316	209
Crude oil (g.)	38.2	36.1
Crude oil %	12.1	17.3
Saponification equivalent	286.2	288.5
Free acid (as oleic) %	6.9	9.6
Iodine value	89.1	114.8
Non-saponifiable matter %	4.6	5.9

The whole of the fat was saponified and the soap extracted in dilute aqueous solution with ether in order to remove as much non-fatty material as possible; the fatty acids liberated from the soap were somewhat contaminated with resinified matter and also contained lower fatty acids, which were removed as far as possible by evaporation.

The crude mixtures of fatty acids were then treated with lead acetate in alcoholic solution in order to separate petroselinic (and any saturated) acid from ordinary oleic and linoleic acids. The lead salts deposited from the cold alcohol solution were recrystallised from a little ether, and in this way the following three groups of fatty acids were obtained from each of the two original fatty acid mixtures:

Acids	<i>Heracleum sphondylium</i>			<i>Angelica sylvestris</i>		
	g.	Iodine value	Mean equiv.	g.	Iodine value	Mean equiv.
Solids (<i>S</i>), from insoluble lead salts	6.0	66.7	281	6.3	76.1	284
Liquids (<i>E</i>), from lead salts insoluble in } alcohol, but soluble in ether	8.1	107.4	275	4.7	118.0	274
Liquids (<i>A</i>), from lead salts soluble in } alcohol	11.5	128.7	282	16.1	132.0	276
	25.6			27.1		

The acids from the soluble lead salt fractions deposited, on standing, small quantities of a crystalline acid, which was separated and not taken into account in the above lists. It was not obtained in sufficient amount for adequate investigation, but it does not appear to belong to the higher fatty acids; the substance has been encountered again in the similar fractions of acids from the fatty oil of cultivated parsnip, and we hope to make a more detailed examination of it during the work on this fat which is at present in progress.

It will be observed that the mean equivalents of all the groups of fatty acids are fairly close to those of acids of the oleic series; the acids (*E*) and (*A*) were in all cases dark coloured and somewhat contaminated with non-fatty

material, and this is probably the reason for mean equivalents lower than 280 having been recorded in some cases. Unfortunately, the amount of material at our disposal did not permit us to prepare the corresponding methyl esters and purify the latter by fractional distillation. We were able, however, by direct study of the six groups, to establish the identity of several fatty acids which were present, and these results, together with the iodine values of each fraction, enable us to give an estimate of the composition of both the Hogweed and Angelica fatty acids.

Fatty acids from Heracleum sphondylium.

(i) 6.0 g. of solid acids from insoluble lead salts. A portion (2.5 g.) was converted into the potassium salt and oxidised in dilute ice-cold alkaline solution by potassium permanganate [Lapworth and Mottram, 1925]. The acids recovered from this treatment contained a very small quantity of saturated fatty acid, which melted at about 51°; myristic acid was not present (as shown by mixed m.p. determination) and it is assumed that the substance was impure palmitic acid, possibly containing some stearic acid. The main product, consisting of dihydroxystearic acids, was crystallised twice from ethyl acetate, when it melted sharply at 121°; this melting-point was unchanged by admixture with authentic 6 : 7-dihydroxystearic acid prepared from parsley-seed oil.

Another portion (2.1 g.) was dissolved in glacial acetic acid (20 cc.) and treated with 35 % hydrogen peroxide solution (5 cc.). The product, after two crystallisations from ethyl acetate, consisted of white crystals, m.p. 114–115°, this being unaltered by admixture with the corresponding isomeric form of 6 : 7-dihydroxystearic acid prepared from parsley-seed oil.

(ii) 8.1 g. of liquid acids from lead salts separated in ether solution. Oxidation of these acids (4 g.) by the method of Lapworth and Mottram furnished a mixture of dihydroxy- and tetrahydroxy-stearic acids, a small amount of tetrahydroxystearic acid which melted at 168° being isolated. The main product consisted of dihydroxystearic acids, the melting-point of which could not be raised above 109–114° (indef.) by crystallisation from ethyl acetate, chloroform or alcohol; apparently both 6 : 7- and 9 : 10-dihydroxystearic acids were present.

(iii) 11.5 g. of liquid acids from alcohol-soluble lead salts. Similar oxidation of these acids (4.4 g.) gave tetrahydroxystearic acid (m.p. 150–152°) soluble in hot water, tetrahydroxystearic acid (m.p. 173°) insoluble in hot water and crystallised from ethyl acetate, and a fraction, more soluble in ethyl acetate than the preceding, giving a product which melted at 113–114° on further recrystallisation (apparently a mixture of dihydroxy- and tetrahydroxy-stearic acids).

The acids present in the original mixture from Hogweed seeds were thus palmitic, stearic (?), petroselinic ($\Delta^{6:7}$ -octadecenoic), oleic ($\Delta^{9:10}$ -octadecenoic) and linoleic acids.

Fatty acids from Angelica sylvestris.

The corresponding groups of these acids were examined in the same manner as the above with the following results.

(i) 6.3 g. of solid acids from insoluble lead salts. Aqueous alkaline oxidation of the acids (2.7 g.) with permanganate yielded the 6 : 7-dihydroxystearic acid, M.P. 120–121° (unchanged by admixture with the corresponding acid from petroselinic acid of parsley), together with a very small quantity of palmitic acid, which was not obtained quite pure (M.P. 58–59.5°).

Hydrogen peroxide in acetic acid converted the same acids (3.3 g.) into the isomeric 6 : 7-dihydroxystearic acid which melted, after crystallising twice from ethyl acetate, at 112.5–114° (no depression when mixed with an authentic specimen derived from parsley-seed petroselinic acid).

(ii) 4.7 g. of liquid acids from lead salts separated in ether solution. Aqueous alkaline oxidation with permanganate gave a small amount of tetrahydroxystearic acid, which melted at 169°, and a mixture of dihydroxystearic acids which could not be further resolved by crystallisation, and melted indefinitely at 111–114°.

(iii) 16.1 g. of liquid acids from alcohol-soluble lead salts. The aqueous alkaline permanganate oxidation yielded a mixture of hydroxylated acids, including tetrahydroxystearic acid (M.P. 170–171°) and a product similar to that obtained from the corresponding Hogweed fraction, which melted at 111–114° (indef.) and was apparently a mixture of dihydroxy- and tetrahydroxy-stearic acids.

The same acids were thus identified in the *Angelica* as in the *Heracleum* fatty acids.

If we assume that the fatty acid mixtures consist essentially of palmitic, petroselinic, oleic and linoleic acids, it is possible to arrive at a partial estimate of their quantitative compositions; since, however, the results of oxidation indicated fairly clearly that some petroselinic acid had passed into the ether-soluble lead salt fractions (*E*), it must be borne in mind that the petroselinic acid figures stated (which are based only on the solid acids (*S*) which definitely yielded 6 : 7-dihydroxystearic acid) do not represent the total amount of this acid.

Fatty acids of Heracleum sphondylium.

Fraction	g.	Iodine val.	Acid			
			Palmitic	Petroselinic	Oleic	Linoleic
<i>S</i>	6.0	66.7	1.1	4.9	—	—
<i>E</i>	8.1	107.4	—	—	6.6	1.5
<i>A</i>	11.5	128.7	—	—	6.6	4.9
	25.6		1.1	4.9	13.2	6.4
	%		4.3	19.1	51.6	25.0

Fatty acids of Angelica sylvestris.

Fraction	g.	Iodine val.	Acid			
			Palmitic	Petroselinic	Oleic	Linoleic
<i>S</i>	6.3	76.1	1.0	5.3	—	—
<i>E</i>	4.7	118.0	—	—	3.3	1.4
<i>A</i>	16.1	132.0	—	—	8.6	7.5
	27.1		1.0	5.3	11.9	8.9
	%		3.7	19.6	43.9	32.8

Whilst, therefore, petroselinic ($\Delta^{6:7}$ -octadecenoic) acid is present in considerable amount in the seed fats from both *Heracleum sphondylium* and *Angelica sylvestris*, the proportion of this acid is much less than in the case of *Petroselinum sativum* seed fat (76.5 %). Even if a substantial amount of the lead salt of the acid had passed into solution on treatment with ether (lead petroselinate is, as a matter of fact, only sparingly soluble in ether), the amount of petroselinic acid would not be increased to more than 30–40 % of the combined fatty acids.

If it be surmised that petroselinic acid is characteristic of Umbellate seed-fats proper, and that the mericarp fat does not, perhaps, contain the isomeric oleic acid, figures of the order obtained would rather be expected, since the fruits of *Heracleum* and *Angelica* are notable for large mericarps or winged carpels. A decision on this point must be deferred until the studies of parsnip, carrot, celery, chervil and other Umbelliferous seed fats now in progress are further advanced.

REFERENCES.

- Hilditch and Jones (1927). *J. Soc. Chem. Ind.* **46**, 174 T.
Lapworth and Mottram (1925). *J. Chem. Soc.* **127**, 1628.
Möslinger (1877). *Liebig's Ann.* **185**, 26.
Müller (1881). *Ber. deutsch. chem. Ges.* **14**, 2476.
Palazzo and Tamburello (1914). *Atti. R. Accad. Lincei.* (v), **23**, ii, 352.
Scherer (1909). Inaugural Dissertation, Strassbourg.
Vongerichten and Kohler (1909). *Ber. deutsch. chem. Ges.* **42**, 1638.
Zincke (1869). *Liebig's Ann.* **152**, 1.