A Review on Petroselinic Acid and Its Derivatives[1]

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Abstract

This publication contains a comprehensive review of literature on petroselinic acid and its derivatives. All known sources of petroselinic acid including its synthetic derivation have been explored and described. The different plant species, whose seeds offer an oil reported to contain petroselinic acid, have been listed and the amounts of oil and their prevalent fatty acid components given. Its method of isolation from the naturally occurring triglycerides and identification have been discussed. The descriptions of characteristics and properties of petroselinic acid and its various derivatives are also included. In many cases they have been compared to oleic acid and other related fatty acids and their derivatives. The various methods of chemical modification of petroselinic acid have been investigated and the derivatives obtained have been summarized in tabular form. Some potential uses for petroselinic acid and the products obtained from it have also been discussed. This review was designed to show what is known about petroselinic acid to date, and perhaps to create further interest in research on this unique naturally occurring octadecenoic acid.

Introduction

OUR AGRICULTURAL ECONOMY is faced with surpluses of farm products, causing price support programs to become very costly. There is need to develop new economic crops, producing products which would not be competitive with products of crops now in surplus and which could be grown on land now planted with surplus crops such as cotton, wheat, and corn.

Petroselinic acid is relatively rare among octadecenoic acids because its unsaturation occurs in the 6,7-position, whereas oleic acid, which is abundant in most of our present vegetable oils and animal fats, has the unsaturation in the 9,10-position. Since there is this difference in structure, petroselinic acid offers the opportunity to produce chemical derivatives different from those which can be produced from other oils.

This communication presents an overall review of the preparation, properties, and reactions of petroselinic acid with references to all the pertinent literature published through 1961. The review should offer an insight into what is known about petroselinic acid and its chemistry. It is anticipated that it will promote additional interest in research on this unusual octadecenoic acid so it may be utilized further to produce a new variety of unusual compounds.

In screening investigations carried out at the Northern Utilization Research and Development Division, in cooperation with the New Crops Research Branch, Crops Research Division, on composition of potential new oilseed crops, it was determined one of the most promising classes of oilseed for the production of industrial oils would be that oilseed which produces oils high in petroselinic acid.

Discussion

Sources of Petroselinic Acid

More than 50 yr ago Vongerichten and Köhler (136) established the presence of a solid isomeric oleic acid in the fatty oil of parsley seed, determined its constitution as 6,7-octadecenoic acid, and gave it the name petroselinic acid. During the same year Scherer (107) also observed a solid oleic acid (presumably petroselinic acid) in the seed fats of two other plants of the Umbelliferae family; *Pimpinella anisum* L. and *Foeniculum capillaceum* Gilib. Palazzo and Tamburello (87) in 1914, stated that the same acid is present in the fatty oil of *Hedera helix* L. seed of the Araliaceae family. No further work on petroselinic acid was published until 1927, when Hilditch and Jones (42) wrote about "Some Ill-Defined Acids of the Oleic Series" and reported on the composition of English parsley seed oil, and Van Loon (132) described his procedure for the isolation of petroselinic acid from parsley seed of Dutch origin.

The different plant species whose seeds offer an oil reported to contain petroselinic acid are listed in Table I along with the kind and amount of the prevalent fatty acid components.

Many of the references cited in the table contain comparisons of the plants and their chemical constitution. Thus, it may be seen that petroselinic acid is a characteristic component of the seed oil from plants belonging to the Umbelliferae family and the closely related Araliaceae family of the order *Umbellales.* It also occurs in the seed oil of the genus *Picrasma* (*P. quassioides* Benn.) of the family Simarubaceae, the genus *Ternstroemia* (*T. japonica* Thunb.[2]) of the family Ternstroemiacae, and the genus *Mallotus* (*M. japonicus* Muell. Arg.) of the family Euphorbiaceae. It is of interest that this acid is also present in small quantities in the bark of the *Jatropha glandulifera* Roxb. tree also of the family Euphorbiaceae (110) and even in human hair (138).

Just as the oil content of the seed varies with each species, so does the amount of the numerous fatty acid components. Although a great deal of interest has been shown in the analysis and characterization of the various oils containing petroselinic acid, there is need for further research to determine the factors influencing the variations of the petroselinic acid content among varieties of the same plant species.

Of all the seed oils examined, parsley seed oil appears to have the highest content of petroselinic acid. At the present time parsley is cultivated mainly for its foliage. Its principal use is for garnishing meats, fish, and other dishes, and for improving the flavor of soups and gravies. The leaves also have a high content of vitamin C (119). Parsley will with-

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[1] Presented at the Am. Chem. Soc. meeting in Atlantic City, N. J., 1962.

[2] *T. japonica* Thunb. is now *T. gymnanthera* (Wight & Arn.) Sprague.

stand considerable frost and could be grown in the South throughout the year as a biennial or perennial. The plants usually bear better if the leaves are removed a few at a time during its growth. When the plant is a year old, it throws up seed-stalks and produces seed in abundance which is easily gathered and cleaned (4). The seeds are comparatively larger than the carrot and celery seeds and produce more fatty oil (139)):

Parsley	18,000 seeds per ounce	25% oil
Carrot	23,000 seeds per ounce	11–16% oil
Celery	72,000 seeds per ounce	15–17% oil

Thus, it appears that cultivation of parsley could produce an economic crop which would not be in competition with crops now in surplus.

Isolation of Petroselinic Acid

Since petroselinic acid naturally occurs along with other closely related fatty acids as a triglyceride, its isolation in pure form is difficult. The oil is usually extracted from ground seeds with petroleum ether or some other low-boiling hydrocarbon. The Nigaki oil was obtained from the *Picrasma* fruit by pressing (128). In general, the seeds contain an unusually

TABLE I

Fatty Acid Composition of Oils Containing Petroselinic Acid

Source Family, genus and species	Common name	Oil in seed %	Total fatty acids in oil %	Unsaponifiable, %	Component acid, % of total fatty acids					Reference
					Petroselinic	Oleic	Linoleic	Palmitic	Other	
Umbelliferae										
Petroselinum sativum (= P. crispum)	English garden parsley	25	82	18	76	15	6	2	Higher saturated	42
	German garden parsley	16.7	91.7	2.2						40
Apium petroselinum (= Petroselinum crispum)	Dutch garden parsley	19	65	30	69.2	9.2	18.5	3.1[a]	Stearic	132
					69.1	12.3	14.0	4.6[a]	Stearic	122
Foeniculum vulgare	Fennel	16.5	54.5	5	ca. 86		ca. 14			55
Foeniculum officinale (= F. vulgare)	Fennel	9.9	89.8	3.7						40
Foeniculum capillaceum	Fennel	13.3		16.3	60	22	14	4		19
Ferula alliacea	Giant fennel	19.0	92.1	1.9						11
Daucus carota	Wild carrot	15.9		14.2	58	14	24	4		19
	Indian wild carrot	11.9		3.6	55.5	22.8	14.8	6.9		102
	Common carrot	13.1	92.0	1.5						40
Coriandrum sativum	Common-coriander	8.8		10.4	53	32	7	8		19
	Common-coriander	18.8	91.1	2.3						40
	Bulgarian coriander	19.0	91.9	4.1	38.5	37.8	14.0	9.7		105
Apium graveolens	English wild celery	14.4		18.1	51	26	20	3		19
	Indian Karaffs	17	82	6.4	41.1	30.5	9.7	11.7	Resin	26
	Common celery	16.7	93.0	0.8						40
Pastinaca sativa	Garden parsnip	17.3		2.6	46	32	21	1		19
Sium latifolium	Water parsnip	21.8								90
Heracleum sphondylium	Hogweed cow-parsnip	12.1	57.0	38	19.1	51.6	25.0	4.3		43
Heracleum nipponicum		18.0	66.7		x	x	x	x	Petroselaidic	62
Ptychosis ajowan (= Carum copticum)	Ajowan caraway			2.9	41.8	34.8	20.7	2.6		79
	Ajowan weed	22.8	92.6	1.1						40
Carum copticum	Ajowan caraway	29.5		14	48.1	23.9	20.1	5.3	Resin	29
Carum carvi	Caraway	9.0		14.8	26	40	31	3		19
					17.0	60.9	19.6	2.6		140
	Kümmel	14.8	91.1	2.7						40
Seseli indicum	Indian ajmond	20.0	71.5	18.5	46.1	30.9	13.8	6.2	Resin	30
Seseli libanotis	Meadow saxifrage	37.5	83.4		x		x			58
Anethum sowa (= A. graveolens)	Indian dill			8.6	44.8	34.4	13.3	6.7	Saturated	79
Anethum graveolens	Dill	17.2	92.6	1.1						140
Chaerophyllum sativum	Common chervil	11.3		3.3	41.0	0.5	53.5	5.0		19
Anthriscus cerefolium	Garden chervil	13.2	91.9	1.5						140
Anthriscus sylvestris	Woodland beak-chervil				x		x		Petroselaidic	59
Ammi visnaga	Bishop's weed	6.5	84.2	8.6	45.0	28.8	18.6	4.8	Saturated	13,14
	Kellah	5.9	80.6	2.8	49.8	32.1	13.0	5.1		41,118
Cumminum cyminum	Cumin			9.5	21.3	39.3	27.9	3.4	Saturated	79
	Roman kümmel	9.9	91.5	2.1						140
Pimpinella anisetum	Anise	8.2			26.0	61.0	9.6	3.4		10
Pimpinella anisum	Anise	23.5	88.0	3.5	17.5	43.5	25.0		Saturated	104
	Anise	10.4	92.6	1.0	23.6	56.0	17.1	3.3		140
Angelica sylvestris	Woodland angelica	17.3	56.6	34.1	19.6	43.9	32.8	3.7		43
Angelica glabra	Angelica	18.2	75.0		ca. 35		ca. 65	x	Petroselaidic	56
Angelica polyclada	Angelica	13.3	85.0		x		x	x	Petroselaidic	69
Angelica ursina	Wild angelica	19.9	91.6		x		x	x	Petroselaidic	64
Archangelica decurrens		19.5			9.1	40.0	42.5		Saturated	23[a]
Cryptotaenia canadensis		19.2		7.3	x				Stearic	78
Conium maculatum	Poison hemlock	17.1	73.3		x		x		Petroselaidic	60
Phellopterus litoralis	Corkwing	18.2	89.0		x		x	x	Petroselaidic	61
Ligusticum acutilobum	Ligusticum	21.1	89.8		x	x	x	x	Petroselaidic	63
Bupleurum falcatum	Thorowax	11.9	83.4		x		x		Petroselaidic	65
Osmorhiza aristata	Sweetroot	13.3	75.0		x	x	x	x	Petroselaidic	58
Pleurospermum kamtchaticum		41.2	87.5		x	x	x	x		58
Pleurospermum uralense		23.5	93.3	2.0	11.6	41.6	44.0		Saturated	23
Oenanthe stolonifera	Waterdrop wart	23.2	71.8		x					67
Myrrhis odorata	European sweet cicely	12.0			x					20
Conioselinum univittatum	Hemlock parsley				x		x		Petroselaidic	57
Araliaceae										
Kalopanax innovans (= Acanthopanax innovans)					x		x			53
Hedera helix	English ivy	20.0	89.0	6.6	62	20	13		Saturated	121
Hedera japonica (= Dendropanax japonicum)	Japanese ivy	19.6	80.0		x	x	x	x	Petroselaidic	70
Panax schinseng	Asiatic ginseng	22.0	90.0		x	x			Petroseladic	71
Aralia elata	Hoary Japanese angelica				x		x	x	Petroseladic	72,53 50,53
Gilibertia trifida		35.2			x		x			
Ternstroemiaceae										
Ternstroemia japonica (= T. gymnanthera)		43.3			x		x	x	Saturated	50
Euphorbiaceae										
Mallotus japonicus	Kamala tree	45.8			x		x	x	Myristic	51
Simarubaceae										
Picrasma quassioides	India quassia wood	45.6	76.0	1.5	x	x	x	x	Linolenic, Lauric	128

[a] Including higher saturated acids.

x Present but amount not given.

large proportion of non-fatty material, frequently of a resinous character, which is extracted under the same conditions as the fat. This adds to the complexity of isolating the individual fatty acids in pure form. A mixture of the various free fatty acids may be liberated from the triglyceride by subjecting the oil to saponification after the hydrocarbon extraction solvent has been removed. Skellon and Spence (115) have devised a method whereby the oil is extracted from the crushed seeds and simultaneously saponified by a solution of potassium hydroxide in water, acetone, and alcohol.

The separation of the mixed fatty acids into individual fatty acid components varies. Palazzo and Tamburello (87) found that the fatty acids of ivy seed oil contained components which gave lead salts soluble in ether, along with a component which produced an ether insoluble lead salt which on analysis proved to be petroselinic acid. Later the methods of Twitchell (129) or Lovern (73) were employed for the separation of the mixed fatty acids into liquid and solid fractions. By these procedures the crude mixture of fatty acids is treated with lead acetate in an alcoholic solution. From the cooled alcoholic solution, it is then possible to remove petroselinic acid along with saturated acids in the form of solid lead salts. Some workers have distilled their fatty acids in the form of methyl esters prior to the precipitation of solid lead salts, while others have converted each group of acids into methyl esters after the lead salt precipitation and then submitted these to the fractional distillation at reduced pressure.

Vanin and Chernoyarova (131) isolated petroselinic acid in 32% yield by centrifuging the mixed fatty acids from coriander oil and then recrystallizing the solid fraction from ethanol. However, from their reported melting point (32–33C) and iodine value (I.V.) (88.75) it appears that their product contained a small amount of saturated fatty acids in addition to petroselinic acid.

In another attempt to isolate fractions rich in petroselinic acid, the mixed fatty acids of coriander seed oil were complexed with urea and fractionally crystallized, employing methanol as a solvent (109). Although the procedure utilized five crystallizations of the urea complexes, the petroselinic acid finally isolated was still rather impure as judged from its I.V. of 84.1 (theoretical, 89.9).

Recently, highly purified petroselinic acid was prepared by first crystallizing the component fatty acids from parsley seed oil in 90% ethanol at −25C and then subjecting the product to urea segregation for the removal of the saturated components (35). Employing this procedure, it was possible to obtain petroselinic acid of high purity having a melting point of 29.5–30.1C and an I.V. of 89.4.

Identification of Petroselinic Acid

When the component fatty acids are separated from the mixture, the individual fractions may be characterized and their content identified by various means.

The position of the double bond in the monounsaturated acids is usually determined by cleavage of the ethylenic linkage by oxidation either with potassium permanganate (7,41,42,78,109,128), or ozone and hydrogen peroxide (7,15,25,35,121,132). The resulting monobasic and dibasic acids are then separated and qualitatively or quantitatively characterized either by their melting points or by their chromatographic properties. Thus, oxidative cleavage of petroselinic acid gives lauric and adipic acids while oleic acid yields pelargonic and azelaic acids.

The position of the double bond in methyl esters of octadecenoic acids has also been determined by the addition of deuterium to the ethylenic linkage, followed by the comparison of the mass spectra of the dideuterated compounds with that of methyl stearate (82).

In most cases, however, the 6,7- and 9,10-dihydroxystearic acids have been prepared and identified by their melting points (14,19,26,29,30,41,42,43,50,51, 55,56,57,59,60,61,62,63,64,67,69,70,78,102,110,136) or further oxidized with lead tetraacetate (79) or periodic acid (28) to yield adip- or azelaldehydic acid and lauraldehyde or pelargonaldehyde from petroselinic or oleic acids, respectively. Since the *trans* isomers of petroselinic and oleic acids produce dihydroxystearic acids, which have different melting points than those from the corresponding *cis* isomers this method has an additional value.

The linoleic acid component has been identified either by isolating the tetrabromo derivative having a melting point of 114–115C, (14,29,41,51,121) or the tetrahydroxy derivative which has a melting point of 173C (19,26,29,30,43,55,56,57,59,60,61,62,63,64,65, 67,69,70).

Chromatography of the hydroxamic acid derivatives was devised as another method of estimation of the amounts of the different unsaturated fatty acid constituents in oils (57,58,61,62,63,64,65,68,69,70).

A method for the quantitative determination of saturated fatty acids in oils has been developed in which the unsaturated acids are oxidized with performic acid and the remaining saturated acids are separated and analyzed by chromatography (33).

Preparation of Petroselinic Acid by Synthetic Means

Petroselinic acid may be obtained synthetically by partial reduction of tariric (6-octadecynoic) acid which naturally occurs in the seed oil of *Picramnia* "Sow"[3] (*Picramnia* Sw.) of the Simarubaceae family (123). The synthetic preparation of tariric and petroselinic acids has also been reported by two other routes (5,74,75).

It would be interesting to compare the chemical processes involved in the natural formation of tariric acid in the seed oil of *Picramnia* Sw. with those involved in the natural formation of petroselinic acid in the seed oil of *Picrasma quassioides* since both species belong to the same family. Such research could supply valuable information on the conditions necessary for the synthesis of petroselinic acid in higher amounts in seed oils of other plant species as well as in the laboratory.

Properties of Petroselinic Acid

Since petroselinic acid has been isolated a great deal of interest has been shown in characterizing it and in investigating its properties. Some of the physical constants characterizing the various oils and the petroselinic acid obtained from them are listed in Table II.

In the studies of other characteristics of petroselinic acid many of its properties have been compared to those of its *trans* isomer, and other octadecenoic acids,

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[3] The author is indebted to Quentin Jones of New Crops Research Branch, Crops Research, ARS, USDA for clarification of this plant name. *Picramnia* "Sow" is not a validly published name and hence should not be used. Apparently someone has taken *Picramnia* Sw. (abbreviation for Swartz who named the genus) and decided that this was a name for a species. Somehow the "o" got inserted between the two consonants. We cannot tell which species of *Picramnia* was used in studies by Steger and Van Loon.

TABLE II

Characteristics of Petroselinic Acid-Containing Seed Fats

Seed fat	MP C	Sap. No.	I.V.^{a}	n$_D$–C	Sp. Gr.–C	Acid V^{b}	Other	Reference
Petroselinum sativum								
—tripetroselinin	32	191.2	84.3	1.4619–40				136
—petroselinic acid from	33–4			1.4533–40	0.8681–40			136
—oil		176.5	109.5 (W)	1.4778–35	0.9243–15	3.4		40
—mixed fatty acids from	—7 to 8		108.2 (W)	1.4679–35		180.1		40
—petroselinic acid from	30		90.0				281–2 (N.E.)	115
Petroselinum apium^{c}								
—oil		129.7	121.1 (W)	1.4800–40	0.9663–20	3.2	1.09 (R.M.)	132
—mixed fatty acids from	26		96.6 (W)	1.4597–40		188.0		132
—petroselinic acid from	29.4		89.9 (W)	1.4534–40	0.8802–35	198.7	86.93 (M.R.)	132
Foeniculum-vulgare								
—petroselinic acid from	32–33		90.2			202.0		55
Foeniculum capillaceum								
—oil		181.0	87.9			16.9		19
Foeniculum officinale (= *F. vulgare*)								
—oil		181.2	99.0 (W)	1.4795–35	0.9304–15	2.8		40
—mixed fatty acids from	1–2		98.8 (W)	1.4710–35		180.5		40
Ferula alliacea								
—oil		189.6	90.7 (W)	1.4691–40	0.9156–31.5	16.6	1.81 (R.M.)	11
Daucus carota								
—oil		182.0	106.4			8.0		19
—oil		184.5	97.4 (W)		0.9224–30	7.7		102
—mixed fatty acids from			100.3 (W)			200.0	280.5 (N.E.)	102
—oil		179.4	105.1 (W)	1.4723–30	0.9296–15	2.1		40
—mixed fatty acids from	—1 to 2		102.7 (W)	1.4625–35		179.0		40
Coriandrum sativum								
—oil		193.5	89.5			28.6		19
—oil	17–19	194.0	84.5	1.4676–30		5.1	72.4 (SCN) 0.55 (R.M.)	105
—mixed fatty acids from	24.5–25.0		96.1	1.4598–30		205.0	83.5 (SCN)	105
—oil		182.0	99.8 (W)	1.4704–30	0.9284–15	1.3		40
—mixed fatty acids from	3–4		98.6 (W)	1.4593–35		179.6		40
—oil		192.2	93.8	1.4688–26	0.9190–15	7.8	0.49 (R.M.)	83
—mixed fatty acids from			97.5	1.4678–26		196.5		83
—petroselinic acid from	32–3		88.8	1.4536–47	0.8824–35		86.76 (M.R.)	131
—petroselinic acid from	32.5–33		91.0	1.5250–40	0.9017–40		199.1 (N.E.)	133
Apium graveolens								
—oil		192.0	129.1			5.7		19
—oil		193.2	90.0 (H)	1.4803–25	0.9282–25			26
—mixed fatty acids from			82.0 (H)			199.9		26
—oil		178.1	94.8 (W)	1.4783–35	0.9236–15	1.8		40
—mixed fatty acids from	—2		93.4 (W)	1.4778–35		177.2		40
—petroselinic acid from	30		89.6			198		27
Pastinaca sativa								
—oil		205.8	92.7			12.7		19
Sium latifolium								
—oil		214.3	111.3					90
Heracleum sphondylium								
—oil		195.6	89.1					43
Ptychosis ajowan (*Carum copticum*)								
—oil		189.3	101.3 (H)					79
—oil		176.8	108.8 (W)	1.4710–35	0.9267–15	3.9		40
—mixed fatty acids from	4–5		109.2 (W)	1.4650–35		178.0		40
Carum copticum								
—oil		145.8	103.1 (H)	1.4694–25	0.9202–25	4.0		29
—mixed fatty acids from			103.7 (H)			199.8	84.0 (SCN)	29
Carum carvi								
—oil		186.2	112.1			9.9		19
—oil		178.3	128.5 (W)	1.4710–35	0.9268–15	2.9		40
—mixed fatty acids from	—7		124.6 (W)	1.4679–35		182.8		40
Seseli indicum								
—oil		148.6	82.1	1.4360–31	0.9011–31			30
—mixed fatty acids from			97.6			201.9	277.3 (N.E).	30
Anethum sowa (= *A. graveolens*)								
—oil		173.4	93.5 (H)					79
Anethum graveolens								
—oil		176.0	119.6 (W)	1.4795–35	0.9292–25	3.1		40
—mixed fatty acids from	5		114.2 (W)	1.4760–35		181.0		40
Chaerophyllum sativum								
—oil		189.6	139.4			1.7		19
Anthriscus cerefolium								
—oil		183.1	110.2 (W)	1.4672–35	0.9265–15	1.0		40
—mixed fatty acids from	4–6		115.7 (W)	1.4580–35		183.2		40
Ammi visnaga								
—oil		200.8	100.1 (H)	1.4766–23	0.9377–22	2.7	13.7 (R.M.)	14
—mixed fatty acids from			100.7 (H)			197.9		14
—petroselinic acid from	30		89.5 (H)					14
Cuminum cyminum								
—oil		183.4	94.3 (H)					79
—oil		179.3	91.8 (W)	1.4720–30	0.9256–15	3.3		40
—mixed fatty acids from	—1		90.1 (W)	1.4748–35		181.6		40
Pimpinella anisum								
—oil		185.0	89.3 (K)	1.4737–30		7.1	1.65 (R.M.)	104
—mixed fatty acids from			99.0 (K)	1.4650–30		213.0	75.1 (SCN)	104
—oil		178.4	108.6 (W)	1.4738–15	0.9232–15	1.9		40
—mixed fatty acids from	1–2		110.0 (W)	1.4710–35		180.5		40
Angelica sylvestris								
—oil		194.1	114.8					43
Pleurospermum uralense								
—oil		188.0	118.0		0.9244–20	5.8		23^{a}
Cryptotaenia canadensis								
—oil		173.5	127.6		0.9326–15	10.3		78
Myrrhis adorata								
—petroselinic acid from	29–30			1.4565–25			148–52^{c}	20
Hedera helix								
—oil		181.1	102.2 (W)	1.4670–40	0.9151–31	11.0	1.0 (R.M.)	121
—mixed fatty acids from	23–24		97.2 (W)	1.4592–40		199.0	85.4 (SCN)	121
—petroselinic acid from	29.4		89.8 (W)	1.4527–40		198.2	89.5 (SCN)	121

TABLE II (continued)

Characteristics of Petroselinic Acid-Containing Seed Fats

Seed fat	MP C	Sap. No.	I.V.[a]	n_D–C	Sp. Gr.–C	Acid V[b]	Other	Reference
Hedera japonica								
(= *Dendropanax japonicum*)								
—petroselinic acid from	28–29		87.3			200.4		70
Gilibertia trifida								
—oil		163.9	89.5	1.4644–25	0.9137–30	4.0		50
Ternstroemia japonica								
(= *T. gymnanthera*)								
—oil		156.6	98.0	1.4650–25	0.9166–20	1.2		50
Mallotus japonicus								
—oil		194.8	114.8	1.4897–37	0.9354–40	42.1		51
Picrasma quassioides								
—oil		200.5	76.7(W)	1.4712–20	0.9322–20	19.0	1.21(R.M.)	128
—mixed fatty acids from			79.5(W)			207.0		128
—petroselinic acid from	29.0–29.5		86.0(W)			199.7		128

[a] Theoretical I.V. of pure petroselinic acid is 89.9.
[b] Theoretical Acid Value of pure petroselinic acid is 200.4.
[c] Not a validly published name.
[d] B.P. at 0.5 mm pressure.
N.E. = Neutralization equivalent (Theoretical for pure petroselinic acid is 282.5).

R.M. = Reichert-Meissl Value.
M.R. = Molecular Refractivity.
SCN = Thiocyanogen Value.
W = Wijs method.
H = Hanus method.
K = Kaufmann method.

especially oleic and elaidic acids. Following is a summary of various properties attributed to petroselinic acid and its derivatives according to investigations reported to date.

The effect of various types of long chain aliphatic molecules as unimolecular films on aqueous solutions has been investigated and the results indicated that increased adhesion for aqueous surfaces corresponding to the increasing dipole moment was exhibited by the different acids in the following order: myristic, oleic, petroselinic, chalmoogric, stearolic, and *alpha, beta-isoöleic* acids (47).

When compared in their melting dilation properties, experiments indicated that dilation increased in the order of oleic, petroselinic, petroselaidic, and elaidic acids. The specific volumes between −17C and 25C increased in the order of elaidic, petroselinic, petroselaidic, and oleic acids (113).

The dialyzing speed of the following fatty monoglycerides in dioxane-water decreased in the order of petroselaidic, petroselinic, elaidic, and oleic monoglycerides (137).

Six C_{18} fatty acids of natural origin having 1–6 double bonds, including petroselinic acid from coriander oil, were isolated as methyl esters and their unsaturation value-refractivity relationships tabulated and graphically presented. The experimental values show very little deviation from the calculated ones indicating that these relationships are dependent on definite structural characteristics of the esters examined (130).

X-ray diffraction studies of *trans*-6-through 12-octadecenoic acids show that those with unsaturation at odd number of carbon atoms from the carboxyl group have greater long spacings and lower melting points. These results have been explained on the basis of the magnitude of the long spacings. It is possible that in the odd ethylenic acid structure, the hydrocarbon chains are perpendicular and that in the even structure, chains are tilted with respect to the carboxyl planes (77,126). Similar results have been obtained in investigations involving the corresponding dihydroxystearic acids. They have been distinguished and also classified in four groups by the relative intensities of their x-ray diffraction spacings (76,124, 126).

Infrared absorption spectra have been described for 19 pure saturated and unsaturated fatty acids, including petroselinic acid, and their esters, triglycerides, and alcohols in the region from 2–15 μ. The absorption bands are also correlated here with the molecular structure of the compounds (112). Absorbances at 10.36 μ have been reported for 17 pure saturated, *cis* and *trans* monounsaturated acids including petroselinic and petroselaidic, and their esters and alcohols (111). Absorption spectra of ferric complexes of oleic, petroselinic, petroselaidic, and erucic hydroxamic acids have also been described (66). The chain segments between the double bond and the carboxyl group of 6-, 7-, 8-, 9-, and 11-octadecenoic acids have been related to infrared bands in the region of 1180–1350 cm^{-1}, and their corresponding dihydroxystearic acids have been studied in the region of 800–1200 cm^{-1} (125). In another paper, the near-infrared spectra of 65 fatty acids and related compounds, including petroselinic acid, have been described in the region from 0.9–3.0 μ and characteristic absorption bands have been assigned to *cis* unsaturation, conjugated double bonds, triple bond, methyl, methylene, hydroxyl, carbonyl, ester, and amine groups (44).

Saturated and unsaturated fatty acids of the same chain length, including petroselinic acid, have been separated by displacement chromatography on a column employing carbon (Darco G 60) as an adsorbent and aqueous ethanol as a solvent (45). Reverse-phase chromatography on a column of water repellent kieselguhr impregnated with paraffin and using acetone-water mixtures with bromothymol blue indicator as an eluent has been employed to separate 7 saturated and 19 unsaturated fatty acids, including petroselinic acid (22,23). The relation between structure and Rf has been discussed in a reverse-phase chromatographic separation of 40 pure fatty acids, including petroselinic acid, employing paper impregnated with paraffin, castor oil, or polyethylene as an adsorbent and acetic acid or acetone as eluting solvents (6).

During the investigation of solubilities of fatty acids in methanol, ethyl acetate, ether, acetone, toluene, and heptane, it was found that the solubility is increased when the chain length of the fatty acid is decreased and when the ethylenic unsaturation is increased. But as the double bond is located closer to the carboxyl group, or when a *cis* olefinic bond is changed to the *trans* configuration or replaced by a triple bond, the solubility of the fatty acid becomes decreased. Thus, the fatty acids examined range from the most soluble to the least soluble in the following order: linoleic, oleic, eicosenoic, petroselinic, stearolic, erucic, elaidic, petroselaidic, palmitic, stearic, brassidic, arachidic, and behenic (52).

It has been known that normal, branched, saturated, and unsaturated fatty acids can be separated from each other by urea complex crystallization. In addition, it has been found that petroselinic acid forms an urea complex more readily than oleic and elaidic acids, but less readily than petroselaidic and stearic acids. Thus, by varying the amounts of urea and methanol, and the temperature of crystallization, it is possible to separate mixtures of C_{18} fatty acids into fractions of component isomers by fractional urea recrystallization (108).

When treated with Kaufman's bromine solution, petroselinic acid and its methyl and butyl esters brominated faster than petroselaidic acid and its esters (127).

During experiments on thiocyanation of fatty acids and their derivatives, petroselinic acid has been 34.6, 30.8, and 99.4% thiocyanated after 5 min, 1 hr, and 1 day, respectively. It was found that the presence of oxygen-bearing groups in the compound, such as, –OH, –CHO, –COR, or –COOH, lowers the rate of thiocyanogen addition to a double bond. When such a group is adjacent to the unsaturation, almost no thiocyanation takes place while a more remote location shows a smaller influence (12).

The rate of hydrolysis of petroselinate esters by alcoholic KOH has been found to be slower than that of the corresponding petroselaidate esters (98).

During comparative studies of hydrogenation of 2-, 3-, 6-, and 9- octadecenoic acids in the presence of platinum black, it was found that the ease of hydrogenation is affected by the position of the double bond; the rate of hydrogenation being faster when the ethylenic linkage is further removed from the carboxyl group (88). Petroselinic acid and its methyl, propyl, and benzyl esters hydrogente faster over platinum black (89) and Pt-$BaSO_4$ (98) than petroselaidic acid and its corresponding esters.

Potassium permanganate oxidation studies employing the method of surface potentials showed that petroselinic acid has a higher oxidation rate than oleic acid, probably due to the closer proximity of the double bond to the carboxyl group (48). Petroselinic acid and its methyl, propyl, and benzyl esters undergo oxidation by potassium permanganate more rapidly than the corresponding petroselaidates, in accordance with the concept of steric hindrance caused by the *trans* ethylenic bond (97,98). Oxidation of 2-, 6-, and 9-octadecenoic acids with benzoyl peroxide indicated that the further the double bond is removed from the carboxyl group the more the oxidation rate constant is increased (89). The same reagent also oxidized the *cis* isomers faster than the corresponding *trans* isomers (89,100). The 2-naphthyl esters were oxidized slower than the methyl esters, and both esters in turn were oxidized slower than the free acids with benzoyl peroxide in actone (100).

The methyl, propyl, and benzyl esters of petroselinic and petroselaidic acids were also prepared by Plisov and Bykovetz (99), who also conducted investigations on their oxidation, hydrogenation, and saponification properties.

Experiments in autoxidation of pure monoethenoid fatty acids showed that various metal soaps of petroselinic and petroselaidic acids are effective catalysts, some being active as accelerators and others as inhibitors, depending on the inherent atomic nature of the metal. It has been found that the configuration of the acid radical of the soap also exerts some influence on certain stages of oxidation, the *trans* isomers being less active as catalysts than the *cis* isomers (114,116). Similar investigations carried out with methyl, ethyl, propyl, and butyl esters of petroselinic acid employing uranyl petroselinate as a catalyst indicated that the reactivity of the petroselinate molecule toward oxygen is decreased as the magnitude of the ester group increases (38).

Investigations of the reaction of petroselinic acid with a hydrochloric acid solution of iodine trichloride and iodine monochloride have shown that the former reagent was less reactive even though both reagents reacted by the same mechanism and formed the same iodochloro derivatives. It was postulated that the iodine trichloride in a solution of hydrochloric acid gave off one molecule of chlorine and the iodine monochloride then added to the ethylenic linkage (32,36).

Reactions of Petroselinic Acid

Due to the similarity in structure, most of the chemical reactions described for oleic acid can readily be adopted for the modification of petroselinic acid. However, the difference in the proximities of the ethylenic linkages to the carboxyl group often has a great influence on the outcome of some of the reactions employed in the modification of the different positional isomers of the octadecenoic series.

Petroselaidic acid is the stereoisomer of petroselinic acid and in small amounts is a normal constituent of some of the fruit oils where petroselinic acid is the major component (57,58,59,60,61,62,63,64,65,68,69,70,71, 72). Presumably, its quantity present in the natural oil depends on the amount of ultraviolet irradiation from the sun the plant had received prior to harvesting of the fruit (54, 68). In the laboratory, small amounts of HNO_2 (27), or warm 20% HNO_3 containing a small amount of $NaNO_3$ (68) or NO_2 (120), as well as ultraviolet light were found to be effective elaidinization catalysts. The use of selenium catalyst (117) or treatment with heat, alkali, or dilute acids (68) were unsuccessful in the isomerization of petroselinic acd to petroselaidic acid. Griffiths and Hilditch (39) obtained 60% petroselaidic acid from petroselinic acid, 68% elaidic from oleic acid, and 66% methyl elaidate from methyl oleate employing Poulet's reagent (Hg in HNO_3). They found that the elaidinization process is an equilibrium reaction and that the same results are obtained whether the *cis* or *trans* acids are isomerized.

The position of the double bond in the 18-carbon chain can also be altered under the influence of certain reagents, and the direction in which it is shifted from the original position depends on the reaction conditions. For instance, migration of the double bond took place in both directions when methyl petroselinate and petroselaidate were subjected to hydrogenation conditions (9). During the formoxylation of petroselinic acid employing perchloric acid as a catalyst (95) migration of the double bond also took place in both directions, but the shift was more pronounced in the opposite direction from the carboxyl group. This is in contrast to the results obtained when oleic acid was subjected to the same formoxylation conditions and no migration of the double bond was observed in either direction (106). When nickel containing sulfur (8) or nickel carbonate (131) were employed as isomerization catalysts for petroselinic acid and 6(7)-chlorostearic acid, respectively, migration of the double bond occurred only away from the carboxyl group.

Fusion of petroselinic acid with potassum hydroxide yielded 78% palmitic acid and a mixture of octadecenoic acids, the structures of which indicated

TABLE III

Properties of Some Petroselinate and Petroselaidate Esters

Derivative	MP C	B.P. C/mm Hg	n_D–C	d–C	I.V.	Other	Reference
Methyl petroselinate		196–7/8	1.45016–20	0.8767_{4}^{20}		90.76 (M.R.)	15,16
		200–2/4	1.4538–20			188 (S.V.)	38
		140–6/0.5	1.4341–65		84.5		7
n-Propyl petroselinate		199–200/5	1.45317–20	0.8711_{4}^{20}	74.3	100.56 (M.R.)	16
		220–2/4	1.4514–20			173 (S.V.)	38
iso-Propyl petroselinate		192–4/5-6	1.45116–20	0.8688_{4}^{20}	74.4	100.44 (M.R.)	16
iso-Butyl petroselinate		202–4/6-7	1.45267–20	0.8674_{4}^{20}	72.2	105.25 (M.R.)	16
n-Butyl petroselinate		225–7/4	1.4535–20			167 (S.V.)	38
iso-Amyl petroselinate		216–7/5-6	1.45357–20	0.8682_{4}^{20}	67.8	109.7 (M.R.)	16
iso-Octyl petroselinate		236–9/5-7	1.45417–20	0.8652_{4}^{20}	63.1	123.35 (M.R.)	16
Benzyl petroselinate		218/2-3	1.4825–20	0.9315–23°			99
Benzyl petroselaidate		229/2-3	1.4842–20	0.9372–23°			99
p-Phenylazophenacyl petroselinate	56–7						135
p-Phenylazophenacyl petroselaidate	78–80						135
Cholesteryl petroselinate			1.4972–20		72.9	$[\alpha]_D^{20}$ –21.9	86
p-Bromophenacyl petroselinate	44–5						20
Glyceryl tri*petroselinate*	26.2				85.9	189.8 (S.V.)	120
Glyceryl tripetroselaidate	50.1				85.9		120

M.R. = Molecular Refractivity.
S.V. = Saponification Value.

migration of the ethylenic bond from the 6,7-position toward as well as away from the carboxyl group. Comparison of this reaction with the alkali fusion of other isoöleic acids showed that the rate of reaction increases with the proximity of the double bond to the carboxyl group (1). Potassium hydroxide fusion of 6-oxostearic acid derived from petroselinic acid produced small amounts of tridecanoic and adipic acids in addition to the main products, 3-dodecyladipic and 2,3-trimethylene-2-pentadecenoic acids. The latter gave 3-dodecyladipic acid on further fusion with potassium hydroxide (24).

It was found that hydroperoxides were formed at the 5th, 6th, 7th, and 8th carbon position in the chain of the various esters of petroselinic acid when subjected to autoxidation experiments catalyzed by uranyl petroselinate, indicating migration of the double bond (38).

Conjugated fatty acids in 30–40% yields have been obtained from the methyl esters of oleic, petroselinic, erucic, stearolic, and behenolic acid by bromination with N-bromosuccinimide employing dibenzoyl peroxide as a catalyst and followed by thermal dehydrobromination (20,81). The resulting compounds having conjugated double bonds were characterized by ultraviolet absorption spectra, iodine numbers, diene values, and hydrogenation data (81).

Petroselinic and petroselaidic acids have been subjected to many types of reactions, and as a result many new derivatives have been prepared. In Table III are listed along with some of their properties, the esters of petroselinic and petroselaidic acids that have appeared in literature up to date.

In addition to the esters, the following metal soaps of petroselinic and petroselaidic acids have been prepared: uranyl (UO_2–), thorium, cerium, and cobalt (116), lithium, copper, silver, magnesium, zinc, cadmium, aluminum, thallium, tin, lead, and bismuth (114), and barium (136).

Some other products obtained and their method of preparation in experiments where the entire molecule of petroselinic acid or its derivatives was subjected to chemical modifications are summarized in Table IV which contains the halogen derivatives, Table V the oxygen derivatives, and Table VI the nitrogen derivatives of petroselinic and petroselaidic acids and their derivatives. It is interesting to note that the various reagents employed in the preparation of some of the derivatives have a different directing influence on the reactive ethylenic linkage of petroselinic acid and its *trans* isomer. For instance, it was found that performic (31) and peracetic acids (20, 28,79), and anhydrous silver iodide dibenzoate (103) oxidize the *cis*-petroselinic acid to the lower melting *threo*-6,7-dihydroxystearic acid, while peracetic acid in the presence of osmium tetroxide (28), iodine and silver acetate in acetic acid (28), potassium permanganate (28,49,120,133), or silver iodide dibenzoate in the presence of water (103) produce the higher melting *erythro*-6,7-dihydroxystearic acid. Similarly, the lower melting 6,7-epoxystearic acid may be obtained from *cis*-petroselinic acid by use of the usual epoxi-

TABLE IV

Halogen Derivatives of Petroselinic and Petroselaidic Acids

No.	Derivative	MP C	Starting material	Reagents	Reference
1	6(7)-Chloro-7(6)-hydroxystearic acid	59–60	Petroselinic acid	NaOCl or HOCl	31
2	6(7)-Chloro-7(6)-hydroxystearic acid	55–56	Petroselaidic acid	NaOCl or HOCl	31
3	6(7)-Chloro-7(6)-hydroxystearic acid	59–60	*cis*-6,7-Epoxystearic acid	HCl	31
4	6(7)-Chloro-7(6)-hydroxystearic acid	55–56	*trans*-6,7-Epoxystearic acid	HCl	31
5	6(7)-Bromo-7(6)-hydroxystearic acid	36–37	Petroselinic acid	NaOBr or HOBr	31
6	6(7)-Bromo-7(6)-hydroxystearic acid	55–56	Petroselaidic acid	NaOBr or HOBr	31
7	6(7)-Bromo-7(6)-hydroxystearic acid	36–37	*cis*-6,7-Epoxystearic acid	HBr	31
8	6(7)-Bromo-7(6)-hydroxystearic acid	55–56	*trans*-6,7-Epoxystearic acid	HBr	31
9	6(7)-Iodo-7(6)-hydroxystearic acid	69–70	Petroselinic acid	I_2, HgO	31
10	6(7)-Iodo-7(6)-hydroxystearic acid	56–57	Petroselaidic acid	I_2, HgO	31
11	6(7)-Iodo-7(6)-hydroxystearic acid	69–70	*cis*-6,7-Epoxystearic acid	HI	31
12	6(7)-Iodo-7(6)-hydroxystearic acid	56–57	*trans*-6,7-Epoxystearic acid	HI	31
13	7-Chlorostearic acid	38–39	Petroselinic acid	HOAc, dry HCl	131
14	Methyl 7-chlorostearate	214/7[a]	Methyl petroselinate	HCl, EtOH	16
15	*n*-Propyl 7-chlorostearate	228/9[a]	*n*-Propyl petroselinate	HCl, EtOH	16
16	*iso*-Butyl 7-chloropetroselinate	229/10[a]	*iso*-Butyl petroselinate	HCl, EtOH	16
17	*iso*-Octyl 7-chloropetroselinate	254/9[a]	*iso*-Octyl petroselinate	HCl, EtOH	16
18	7-Bromostearic acid	50.5	Petroselinic acid	HBr, AcOH	93
19	6,7-Dibromostearic acid	35.5–36, 37-38	Petroselinic acid	Br_2	133, 2
20	6,7-Dichlorostearic acid	74–75	Petroselinic acid	Cl_2	18
21	6(7)-Chloro-7(6)-hydroxystearic acid	Viscous oil	6,7-Dihydroxystearic acid	PCl_5	18
22	6,7-Dichlorostearic acid	66–67	Petroselaidic acid	Cl_2	18
23	Petroselinoyl chloride	144–6/2[a]	Petroselinic acid	$SOCl_2$	20
24	Petroselinoyl chloride	156/3[a]	Petroselinic acid	$SOCl_2$	136

[a] C/mm Hg

TABLE V

Oxygen Derivatives of Petroselinic and Petroselaidic Acids

No.	Derivative	MP, C	Starting material	Reagents	Ref.
25	*threo*-6,7-Dihydroxystearic acid	115–6	Petroselinic acid	HCO_3H	31
26	*erythro*-6,7-Dihydroxystearic acid	122	Petroselaidic acid	HCO_3H	31
27	6,7-Dihydroxystearic acid	114–5, 115–6, 115–7	Petroselinic acid	AcOH, H_2O_2	28, 20, 79,
28	6,7-Dihydroxystearic acid	122	Petroselaidic acid	AcOH, H_2O_2	28
29	6,7-Dihydroxystearic acid	122	Petroselinic acid	AcOH, H_2O_2, OsO_4	28
30	6,7-Dihydroxystearic acid	116	Petroselaidic acid	AcOH, H_2O_2, OsO_4	28
31	6,7-Dihydroxystearic acid	122	Petroselinic acid	AcOH, AcOAg, I_2	28
32	6,7-Dihydroxystearic acid	115–6	Petroselaidic acid	AcOH, AcOAg, I_2	28
33	6,7-Dihydroxystearic acid	122	Petroselinic acid	Neutral $KMnO_4$	28
34	6,7-Dihydroxystearic acid	115–6	Petroselaidic acid	Neutral $KMnO_4$	28
35	*erythro*-6,7-Dihydroxystearic acid	124–5, 122.2	Petroselinic acid	Alkaline $KMnO_4$	49, 120
36	6,7-Dihydroxystearic acid	117	Petroselaidic acid	Alkaline $KMnO_4$	120
37	6,7-Dihydroxystearic acid	121–2, 121.5–122	Petroselinic acid	Alkaline $KMnO_4$	14, 133
38	*threo*-6,7-Dihydroxystearic acid	116–7	Petroselinic acid	$(BzO)_2AgI$ (anhyd.)	103
39	*erythro*-6,7-Dihydroxystearic acid	122–3	Petroselinic acid	$(BzO)_2AgI$ (in H_2O)	103
40	7-Hydroxystearic acid	81.5–82, 82	Petroselinic acid	H_2SO_4	93, 17
41	Ethyl 7-hydroxystearate	37.5	No. 40	NaOEt	93
42	Ethyl 7-hydroxystearate	45–6	Silver petroselinate	C_2H_5I	17
43	Barium 7-hydroxystearate	155	No. 40	BaOH	93
44	Calcium 7-hydroxystearate	131	No. 40	CaOH	93
45	Methyl 6,7-dihydroxystearate	67–8	Methyl petroselinate	AcOH, H_2O_2	28
46	Methyl 6,7-dihydroxystearate	89–90	Methyl petroselaidate	AcOH, H_2O_2	28
47	6(7)-Hydroxy-7(6)-ketostearic acid	67–9, 67–8	Petroselinic acid	Alkaline $KMnO_4$	21, 38
48	6(7)-Hydroxy-7(6)-ketostearic acid	68.5–70	............[a]	Neutral $KMnO_4$	28
49	6-Hydroxy-7-ketostearic acid	74.5–75, 78–9, 74	Via semicarbazones from No. 47 or 48		28, 21, 37
50	7-Hydroxy-6-ketostearic acid	77.5–78.5, 75–6, 75	Via semicarbazones from No. 47 or 48		28, 21, 37
51	Semicarbazone of No. 49	138–9, 141–2, 153	No. 49	Semicarbazide	28, 21, 37
52	Semicarbazone of No. 50	118–9, 116–7, 138	No. 50	Semicarbazide	28, 21, 37
53	*cis*-6,7-Epoxystearic acid	59–60, 59.5–60	Petroselinic acid	AcO_2H	31, 27
54	*trans*-6,7-Epoxystearic acid	66–7, 65.5–66	Petroselaidic acid	AcO_2H	31, 27
55	*cis*-6,7-Epoxystearic acid	60–1, 59–59.5	Petroselinic acid	AcO_2H	49, 94
56	*trans*-6,7-Epoxystearic acid	67–8, 66	Petroselaidic acid	AcO_2H	49, 92
57	*cis*-6,7-Epoxystearic acid	58.5–59.3	Petroselinic acid	AcO_2H	34
58	*cis*-6,7-Epoxystearic acid	59.5–60, 60–1	Petroselinic acid	Monoperphthalic acid	27, 49
59	*trans*-6,7-Epoxystearic acid	66–66.5, 67–8	Petroselaidic acid	Monoperphthalic acid	27, 49
60	*cis*-6,7-Epoxystearic acid	60	Petroselinic acid	Perbenzoic acid	49
61	*trans*-6,7-Epoxystearic acid	67	Petroselaidic acid	Perbenzoic acid	49
62	*cis*-6,7-Epoxystearic acid	59–60	No. 1, 5 or 9 (Table IV)	KOH	31
63	*trans*-6,7-Epoxystearic acid	66–7	No. 2, 6 or 10 (Table IV)	KOH	31
64	*cis*-6,7-Epoxystearic acid	59–60	Petroselinic acid	Via chlorohydrins	27
65	*trans*-6,7-Epoxystearic acid	66	Petroselaidic acid	Via chlorohydrins	27
66	Methyl *cis*-6,7-epoxystearate	25–25.5	No. 64	Diazomethane	27
67	Methyl *trans*-6,7-epoxystearate	23–4	No. 65	Diazomethane	27
68	Methyl *cis*-6,7-epoxystearate	25–25.5	Methyl petroselinate	Monoperphthalic acid	27
69	Methyl *trans*-6,7-epoxystearic acid	23–4	Methyl petroselaidate	Monoperphthalic acid	27
70	Methyl *cis*-6,7-epoxystearate	26.4	Methyl petroselinate	Perbenzoic acid	120
71	Methyl *trans*-6,7-epoxystearate	26.4	Methyl petroselaidate	Perbenzoic acid	120
72	*cis*-6,7-Epoxystearic acid	59–59.5, 59.2	No. 66, 68 or 70	Cold KOH	27, 120
73	*trans*-6,7-Epoxystearic acid	66, 65.4	No. 67, 69, or 71	Cold KOH	27, 120
74	6,7-Dihydroxystearic acid	115–6	No. 66 or 68	Hot KOH	27
75	6,7-Dihydroxystearic acid	122	No. 67 or 69	Hot KOH	27
76	6,7-Dihydroxystearic acid	117	No. 72	Conc. H_2SO_4	120
77	6,7-Dihydroxystearic acid	122	No. 73	Conc. H_2SO_4	120
78	*threo*-6,7-Dihydroxystearic acid	115–6, 118–9	No. 55 or 58	Acid Hydrolysis	27, 49
79	*erythro*-6,7-Dihydroxystearic acid	120–2	No. 56 or 59	Acid Hydrolysis	27
80	*trans*-6,7-Epoxystearic acid	67	No. 78 or 25	AcOH, HBr	49, 31
81	*cis*-6,7-Epoxystearic acid	60	No. 35 or 26	AcOH, HBr	49, 31
82	6,7-Diketostearic acid	97–8	No. 28, 49 or 50	AcOH, CrO_3	28
83	2,4-Dinitrophenylosazone	160	No. 82, 49 or 50	2,4-Dinitrophenylhydrazine	28
84	Dioxime of No. 82	171–2	No. 82	$NH_2OH\cdot HCl$	28
85	6(7)-Hydroxy-7(6)-ketostearic acid	67–69, 69–70	No. 82, 88	AcOH, Zn	21, 28
86	6(7)-Hydroxy-7(6)-ketostearic acid	64–7	No. 35	(NBS), EtOAc, reflux	21
87	6(7)-Hydroxy-7(6)-ketostearic acid	64–7	No. 78	(NBS), EtOAc, rm. temp.	21
88	6,7-Diketostearic acid	90–100	No. 35 or 78	(NBS), EtOAc, reflux, CO_2 atm	21
90	6(7)-Hydroxystearic acid	73–4	No. 55 or 56	AcOH, 10% Pd/C, H_2	49
91	6(7)-Ketostearic acid	75–6	No. 90	AcOH, CrO_3	49
92	Semicarbazone of No. 91	115–6	No. 91	Semicarbazide	49
93	6(7)-Hydroxystearic acid	68–70	No. 57	EtOH, 10% Pd/C, H_2	34
94	*trans*-7,8-Octadecenoic acid	52	No. 18 (Table IV)	KOH, EtOH	93
95	*trans*-7,8-Epoxystearic acid	65.5	No. 94	AcO_2H	93
96	Dihydroxystearic acid	122	No. 95	Hydration	93
97	7,8-Octadecenoic acid	51–2	No. 13 (Table IV)	$NiCO_3$	131
98	Methyl 7,8-octadecenoate	193/8 [b]	No. 14 (Table IV)	$NiCO_3$	16
99	*n*-Propyl 7,8-octadecenoate	205–8/10 [b]	No. 15 (Table IV)	$NiCO_3$	16
100	*iso*-Butyl 7,8-octadecenoate	219/10 [b]	No. 16 (Table IV)	$NiCO_3$	16
101	*iso*-Amyl 7,8-octadecenoate	220–2/8 [b]	*iso*-Amyl petroselinate	HCl, $NiCO_3$	16
102	6,7-Octadecynoic acid (tariric)	50.5	No. 19 (Table IV)	KOH, H_2SO_4	2
103	Methyl 6,8-octadecadienoate	154–6/0.1 [b]	Methyl petroselinate	(NBS), $(BzO)_2$	20
104	6,8-Octadecadienoic acid	153–5/0.1 [b]	No. 103	Hydrolysis	20
105	Methyl 8-hydroxypetroselinate	132–4/0.2 [b]	Methyl 8-bromopetroselinate	Ag_2O, H_2O	20
106	8-Hydroxypetroselinic acid	160–1/0.5 [b]	No. 105	Hydrolysis	20
107	*cis*-6-Octadecene-1-ol	142–3/0.5 [b]	Methyl petroselinate	$LiAlH_4$	20
108	*cis*-6-Octadecene-1-ol	29–30	Petroselinic acid	$LiAlH_4$	49
109	*trans*-6-Octadecene-1-ol	42–3	Petroselaidic acid	$LiAlH_4$	49
110	Hydrogen phthalate of No. 108	30–2	No. 108	Phthalic anhydride	49
111	Hydrogen phthalate of No. 109	42–4	No. 109	Phthalic anhydride	49
112	1,6(7)-Octadecanediol	66–66.5, 69–70	No. 55	$LiAlH_4$, ether	94, 49
113	1,6(7)-Octadecanediol	68–70	No. 55 or 56	$LiAlH_4$, tetrahydrofuran	49
114	1,6(7)-Octadecanediol	69–70	No. 90 or 91	$LiAlH_4$, ether	49
115	7-Ketostearic acid	73.5–74.5	No. 112	AcOH, CrO_3	94
116	Ethyl 7-ketostearate	37	No. 115	NaOEt	94
117	*trans*-6,7-Epoxyoctadecane-1-ol	56–8	No. 56	$LiAlH_4$, ether	49
118	*trans*-6,7-Epoxyoctadecane-1-ol	56–8	No. 109	Perbenzoic acid or AcO_2H	49
119	*erythro*-Octadecane-1,6,7-triol	131–2	No. 35 or [c]	$LiAlH_4$	49
120	*threo*-Octadecane-1,6,7-triol	85–7	No. 78 or [d]	$LiAlH_4$	49
121	*erythro*-Octadecane-1,6,7-triol	131–2	No. 110	Alkaline $KMnO_4$	49
122	*threo*-Octadecane-1,6,7-triol	85–6	No. 111	Alkaline $KMnO_4$	49
123	*erythro*-Octadecane-1,6,7-triol	131–2	No. 109	HCO_2H, H_2O_2	49
124	*threo*-Octadecane-1,6,7-triol	85–6	No. 108	HCO_2H, H_2O_2	49

[a] Petroselinic or petroselaidic acids.

[b] BP, C/mm Hg.

[c] Methyl *erythro*-6,7-dihydroxystearate.

[d] Methyl *threo*-6,7-dihydroxystearate.

(NBS) N-Bromosuccinimide.

TABLE VI

Nitrogen Derivatives of Petroselinic and Petroselaidic Acids

No.	Derivative	MP, C	Starting material	Reagents	Ref.
125	6(7)-Nitroso-7(6)-nitritostearic acid	84–5	Petroselinic acid	N_2O_3	133
126	6(7)-Hydroxy-7(6)-aminostearic acid	127	No. 125	PtO_2, H_2	133
127	6(7)-Nitro-7(6)-nitritostearic acid	121–2	Petroselinic acid	N_2O_4	134
128	6-Amino-7-hydroxystearic acid	189–190	No. 56 (Table V)	NH_3	92
129	Hydrochloride salt of No. 128	128–9	No. 128	HCl	92
130	Methyl ester of No. 129	79–81	No. 129	MeONa	92
131	6-Amino-7-hydroxystearic acid	133–4	No. 55 (Table V)	NH_3	91
132	Hydrochloride salt of No. 131	81.5–83	No. 131	HCl	91
133	Petroselinamide	74–5	No. 23 (Table IV)	NH_3	20
134	Petroselinamide	76	No. 24 (Table IV)	NH_3	136
135	Petroselinamide	72–3	Petroselinic acid	Urea	96
136	Petroselinanilide	62–3	No. 23 (Table IV)	Aniline	20
137	Petroselinonitrile	296–8 [a]	Petroselinic acid	NH_3	96
138	Petroselinylamine	18–20	No. 133	$LiAlH_4$	20
139	Petroselinylamine	17, 286[a]	No. 137	Na, BuOH	96
140	Hydrochloride salt of No. 139	115–6	No. 139	HCl	96
141	N-Acetylpetroselinylamine	29	No. 139	$(AcO)_2O$	96

[a] BP at 760 mm Hg.

dation reagents (27,31,34,49,92,94), but the *trans*-6,7-epoxystearic acid was produced when the lower melting *threo*-6,7-dihydroxystearic acid was treated with hydrogen bromide in acetic acid (49) or dry hydrogen chloride (31). Afanasievski in 1915 reported that oxidation of petroselinic acid with Caro's reagent yielded a 6,7-dihydroxystearic acid, m. p. 96–99C which was a stereo-isomer of the acid, m. p. 122C obtained by oxidation of petroselinic acid with potassium permanganate. He also obtained a 6,7-dihydroxystearic acid, m. p. 96–99C and a stereo-isomeric acid, m. p. 120–123C, by oxidation of petroselaidic acid with potassium permanganate, and Caro's reagent, respectively (1a). Although his carbon and hydrogen analyses indicated that the products were dihydroxystearic acids, the melting point of the lower-melting compound was much lower than that ordinarily given for the *threo*-6,7-dihydroxystearic acid, m. p. 115–117C, but was very close to that of 6,7-diketostearic acid, m. p. 97–98C (28). It has been shown that inversion of configuration also takes place during the replacement of a hydroxyl group in a vicinal dihydroxy compound by a halogen atom, and at the time of opening and closing of the epoxide ring during the halohydrin synthesis (31). Thus, the dihydroxy acids may be converted to their stereoisomers by converting them into epoxides via halohydrins, and then hydrolyzing the epoxides to the corresponding dihydroxy acids.

Certain reagents or conditions employed in the formation of the hydroxy derivatives from petroselinic or petroselaidic acids may cause activation of the ethylenic linkage introducing the possibility of producing different types of isomers and in various amounts. When stereoisomers are formed, they may be easily distinguished by their melting points or by their infrared spectra. The presence of positional isomers may be determined by degradation of the hydroxy acids to a mixture of mono- and dicarboxylic acids which can be then readily identified by various standard methods. The procedure employed most frequently in the resolution of the hydroxy acids at the point where the –OH group is attached may be summarized as follows: hydroxystearic acids are oxidized with $CrO_3 \longrightarrow$ ketostearic acids, treated with hydroxylamine hydrochloride $\longrightarrow$ oximes of ketostearic acids, subjected to Beckmann rearrangement $\longrightarrow$ amides, hydrolyzed $\longrightarrow$ mixture of mono- and dicarboxylic acids (along with amines and amino acids). Component acids of the resulting mixture have been analyzed by chromatography (34,95), or isolated by fractional crystallization and identified by their melting points (136). Others have confirmed the structure of their 6,7-dihydroxystearic acids by oxidation with potassium periodate and sulfuric acid with the formation of lauraldehyde and adipaldehydic acid (28). The same reagents oxidize 6-hydroxy-7-ketostearic acid or 7-hydroxy-6-ketostearic acids to lauraldehyde and adipic acid or lauric acid and adipaldehydic acid, respectively (21). Oxidation of 6-hydroxy-7-ketostearic or 7-hydroxy-6-ketostearic acids with lead tetraacetate in acetic acid produces lauric acid and adipaldehydic·acid or lauraldehyde and adipic acid, respectively (28). The same reagent cleaves 6,7-diketostearic or 6-amino-7-hydroxystearic acids into lauric and adipic acids (28) or lauraldehyde and adipic acid, respectively (91,92). When a monohydroxy acid, such as 7-hydroxystearic acid, was subjected to oxidation with chromic acid, the following products were obtained: lauric, undecylic, adipic, and pimelic acids (17).

In addition to the derivatives shown in the tables, a number of other products have been synthesized from petroselinic acid. The acid has been ozonized and the products reduced either with sodium borohydride in ethanol or zinc and acetic acid producing lauryl alcohol and 6-hydroxycaproic acid (36) or lauraldehyde and adipaldehydic acid (46), respectively. Lauryl alcohol and ethyl 6-hydroxycaproate were obtained from the ozonolysis product of ethyl petroselinate with sodium borohydride, as well as by catalytic hydrogenation employing Raney nickel as a catalyst (36). The lauraldehyde and adipaldehydic acid were further treated with hydroxylamine hydrochloride and the resulting oximes reduced by catalytic hydrogenation in the presence of ammonia and ethanol and employing Raney nickel W-5 as a catalyst, producing dodecylamine and 6-aminocaproic acid (46).

Special Properties Attributed to Petroselinic Acid and Its Derivatives

Although the properties of petroselinic acid and its derivatives have been widely investigated, not much interest has been shown in employing any of these unique compounds commercially. A great deal of this disinterest is due to the high cost of production of pure petroselinic acid at this time. Thus, many of the same compounds are produced by chemical reactions with materials from other sources, or are substituted by similar compounds which have similar properties but which are more economical. However, petroselinic acid and some of its derivatives have some special properties which have been only of academic interest so far, but which could make petroselinic acid essential if further investigations are carried out.

It has been found that soap containing sodium petroselinate has similar properties as sodium oleate soap, but the former is better in detergency (80). The silver soap of petroselinic acid displayed outstanding photogenic activity, the silver petroselaidate soap being less active (114). The magnesium soaps have outstanding emulsion-forming properties owing to their great tendency to retain water. This property also makes them good autoxidation inhibitors for unsaturated fatty acids, this power being specially great in the magnesium petroselaidate (114).

The morpholide of parsley seed oil fatty acids was found to be a good plasticizer for polyvinyl chloride resins. They have greater efficiency and impart better low-temperature properties to the plastic than the standard di-2-ethylhexylphthalate, DOP (80a).

Brominated natural fatty acids have been administered experimentally to rats and humans in an effort to obtain a prolonged bromine therapy. In these experiments, organic and inorganic bromine was found in the urine and various tissues, including fat deposits, with no deleterious effects upon the health and growth of the animal tissues. It was shown that esters of 6,7-dibromostearic acid were more readily debrominated and the fat infiltrated the liver of a rat to a higher degree than the esters of 9,10-dibromostearic or 13,14-dibromobehenic acids (3).

A number of long chain fatty acids have been tested for their ability to support the growth of an oleic acid-requiring diphtheroid bacterium, *Corynebacterium "Q"*, in a medium of known composition. It was found that petroselinic acid was less active than oleic acid in promoting growth, none of the saturated fatty acids was active, and linoleic, linolenic, and palmitoleic acids were actually inhibitory (101). It is possible that the 6,8-octadecadienoic acid prepared by Clemo and Stevens (20) would have a similar inhibitory effect.

In another study, ricinoleic, oleic, and petroselinic acids and their derivatives were screened for their antimicrobial activity, under optimum growing conditions, against several species of bacteria, yeasts, and molds. Ricinoleic and petroselinic acids and their derivatives exhibited considerable activity. In some cases, their activity against some microorganisms was comparable to sorbic and 10-undecenoic acids, well known antimicrobial agents (84,85).

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Internal Hydrogen Bonding, Rotational Isomerism and Differentiation of 1,2- and 1,3-Diglycerides by Near Infrared Spectroscopy[1]

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Abstract

The OH stretching modes of 1,2- and 1,3-diglycerides in dilute carbon tetrachloride solution have been investigated in the fundamental and first overtone region with a spectral resolution of about 1 cm^{-1}. The spectra of both position isomers can be interpreted in terms of three predominant configurations: one internally H-bonded and two involving no H-bonds. The fraction of H-bonded molecules appears to be relatively low. The data suggest that the H-bonded form of 1,3-diglycerides has a *trans,gauche* configuration around the glyceride CC bonds, while the non-H-bonded forms probably have a *trans,trans* configuration around the glyceride backbone, OH being either *trans* or *gauche* with respect to the nearest C—H group. In 1,2-diglycerides H-bonds seem to be predominantly formed between groups attached to the α,γ carbons of the glyceride residue, the configuration around the backbone being *trans,trans;* two stretching bands of non-H-bonded OH groups are associated with rotational isomerism around the alcoholic CO bond. The usefulness of OH stretching modes for analyzing mixtures of 1,2- and 1,3-diglycerides is discussed. Reasonably accurate results can be obtained by using either the fundamental or the first overtone region.

Introduction

In a molecule of the general formula CH_2X CHY CH_2Z—which corresponds to a generalized glyceride model where OH and OCOR groups are assumed to be rigid—internal rotation is possible about two carbon to carbon bonds, giving rise to nine rotational isomers. If two or more substituent groups are identical the number of isomers is decreased, but the picture still remains highly complex, as evidenced by recent NMR studies (1). In the case of mono- and diglycerides some isomers are stabilized by internal hydrogen bonding and information regarding rotational isomerism can be obtained by investigating the characteristic OH stretching vibrations which are sensitive to intramolecular environment in general, and hydrogen bonding in particular. The over-all problem is, of course, more complex than the simple model represented by CH_2X CHY CH_2Z suggests, because of hindered rotation around the various C—O bonds and the C—C bonds of hydrocarbon side-chains. The present communication discusses rotational isomerism of 1,2- and of 1,3-diglycerides in dilute CCl_4 solution in the light of observed infrared spectra in the fundamental OH stretching region (around 3500 cm^{-1}) and

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