227. C. Oberberger and J. Anselme, J. Org. Chem., 29, 1188 (1964).
228. W. Ried and H. Lohwasser, Annalen, 683, 118 (1965).
229. E. J. Moriconi and J. J. Murrey, J. Org. Chem., 29, 3577 (1964).
230. S. Masamune, J. Amer. Chem. Soc., 86, 735 (1964).
231. S. Masamune and N. Castellucci, Proc. Chem. Soc., 298 (1964).
232. J. Novak, Coll. Czech. Chem. Comm., 22, 1836 (1957).
233. F. Sorm, Coll. Czech. Chem. Comm., 12, 245 (1947).
234. P. C. Guha, Ber., 71 2665 (1938).
235. W. Treibs, Annalen, 598, 38 (1956).
236. A. Small, J. Amer. Chem. Soc., 86, 2091 (1964).
237. F. Weygand and K. Koch, Angew. Chem., 73, 531 (1961).
238. G. Stork and F. Ficini, J. Amer. Chem. Soc., 83, 4678 (1961).
239. W. von E. Doering, E.T. Fossel, and R. L. Kaye, Tetrahedron, 21, 25 (1965).
240. D. Becker and H. J. E. Loewenthal, Chem. Comm., No. 8, 149 (1965).
241. Yu. A. Zhdanov, V. I. Kornilov, and G. V. Bogdanova, Carbohydrate Res., 3, 139 (1966).
242. V. Ioan, M. Popovici, E. Mosanu, M. Elian, and C. D. Nenitzescu, Rev. Roumaine Chim., 10, 185 (1966).
243. M. Fawzi and D. Gutsche, J. Org. Chem., 31, 1390 (1966).

Leningrad State University

U.D.C. 547.39

CHEMISTRY OF NATURAL ALIPHATIC ACIDS CONTAINING A CONJUGATED SYSTEM OF DOUBLE BONDS

V.D. Solodovnik

CONTENTS

1. Introduction 272
2. General properties and methods of establishing structure 272
3. Dienoic acids 274
4. Trienoic and tetraenoic acids 276
5. Syntheses of naturally occurring polyenoic aliphatic acids. 280

1. INTRODUCTION

Until recently only a very small number of aliphatic acids containing a conjugated system of double bonds had been found in Nature. These acids had been isolated in individual cases from plant lipids, and were regarded in oil and fat chemistry as fairly rare exceptions. The view was even expressed that they might have been formed in the course of isolation, by the isomerisation of unconjugated polyenoic acids. However, several new representatives of this class of compounds have been discovered in recent years, and aliphatic acids containing conjugated double bonds have been shown to be present in the lipids from plants of a great variety of families and species. Sixteen natural conjugated polyenoic aliphatic acids are now known, and the number of natural sources for acids of this type is continually being extended.

Conjugated polyenoic acids form the basis of many long-established film-forming materials. The paint and varnish industry has hitherto made widespread using of drying oils, in which conjugated polyenoic acids either are present in the sodium form (tung oil) or have been formed, as a result of preliminary treatment, from unconjugated polyenoic acids present in linseed or other vegetable oil. In contrast to oils containing unconjugated polyenoic acids, the triglycerides of conjugated acids give valuable varnishes, which dry more rapidly and are more stable to the action of moisture and alkalis.

2. GENERAL PROPERTIES AND METHODS OF ESTABLISHING STRUCTURE

The C_{18} conjugated polyenoic acids most frequently encountered in Nature are colourless crystalline solids. Naturally occurring acids of this type containing a smaller number of carbon atoms in the chain melt below room temperature. They all dissolve well in polar organic solvents, and less well in non-polar solvents.

Polyenoic acids containing *cis*-ethylenic bonds readily isomerise into all-*trans*-isomers under the influence of light and especially in the presence of traces of iodine, sulphur, nitrogen dioxide, and other catalysts.

As a result of the presence of a chromophoric group, conjugated polyenoic acids are able to absorb ultraviolet radiation. Examination of the ultraviolet spectra of stereoisomeric dienoic acids has shown that *trans-trans*-isomers absorb at shorter wavelengths than do *cis-trans*- and *cis-cis*-isomers, the intensity of the absorption maxima diminishing in this sequence. Thus the ultraviolet spectra of the stereoisomeric octadeca-9,11- and -10,12-dienoic acids contain a single maximum at 230, 232, and 234 nm respectively for the *trans-trans*-, *trans-cis*-, and *cis-cis*-isomers[1]. The variation in the position of the absorption maximum and in its intensity is less marked in the spectra of the deca-2,4-dienoic acids, owing to conjugation of the diene group with the carboxyl, but is sufficient to distinguish them[2]. Variations in the ultraviolet spectra are still more marked among the stereoisomers of conjugated trienoic acids, since their spectra contain three absorption maxima (Table 1).

Infrared spectroscopy has an important place in establishing the structure of conjugated polyenoic aliphatic acids. Alkenes of the type RCH:CHR′ are characterised by an intense band at 950–1100 cm^{-1}, due to deformation vibrations

TABLE 1. Ultraviolet spectra of C_{18} conjugated trienoic acids (λ_{max}, nm).

Conjugation	Positions 8, 10, 12	Positions 9, 11, 13	Ref.
cis-trans-cis	265, 275, 287	264, 274, 285	3, 4, 5
		265, 275, 287	5
cis-cis-trans	not known	(264), 271, (279)*	4
cis-trans-trans	261, 271, 232	261, 271, 281	6, 3
trans-trans-cis	262, 272, 283	262, 272, 283	7, 8
trans-trans-trans	259, 269, 280	260, 269, 281	7, 6
	259, 269, 279	259, 268, 279	3, 5

* Values in parentheses relate to an unpurified specimen.

of the *trans*-ethylenic hydrogen atoms, or a band in the range 620–730 cm^{-1} with *cis*-alkenes[9,10], as well as a low-intensity peak in the range 1600–1660 cm^{-1}. These bands may occupy different positions within the above ranges depending on the nature of the substituents R and R′. In particular, the spectrum of elaidic acid contains a band at 968 cm^{-1}, whereas such absorption is absent with oleic acid[11]. The first systematic investigation of the infrared spectra of stereoisomeric conjugated dienoic acids was made on the methyl deca-2,4-dienoates and the corresponding deca-2,4-dienols[2]. Their spectra differed slightly in the position of weak bands in the region of C=C stretching vibrations (~1600 cm^{-1}) but differed very sharply in the region of deformation vibrations undergone by C–H bonds adjacent to ethylenic carbon atoms (940–1100 cm^{-1}) (Table 2).

Table 2 shows that the infrared spectra of the *trans-trans*-isomer contain only one intense band at 950–1010 cm^{-1}, whereas those of all the *trans-cis*-isomers contain also a somewhat less intense band at 950–970 cm^{-1}. The peaks at 1600–1660 cm^{-1} are considerably less intense and are less distinctive of the isomeric dienes.

The infrared spectra of nona-3,5-dienoic[11,12] and trideca-3,5-dienoic[13] acids also exhibit the presence of two bands (at 950 and 980 cm^{-1}) with the *trans-cis*-isomers and of one band in the same range with the *trans-trans*-isomers.

Analogous regularities are observed also in the infrared spectra of conjugated trienoic and tetraenoic acids. Without exception, all the all-*trans*-acids exhibit only one intense band, in the range 1000–940 cm^{-1}. Their isomers, containing both *cis*- and *trans*-ethylenic bonds, usually display two intense peaks in the same range of the infrared spectra (see examples in Table 3) and a band in the range 650–750 cm^{-1} which is characteristic of a *cis*-ethylenic bond. On the photochemical isomerisation of *cis-trans*-isomers into all-*trans*-forms, the peak at 960 cm^{-1} disappears, while the band at 1000 cm^{-1} shifts to 970 cm^{-1}. Thus a qualitative assessment of the character of the infrared spectra of conjugated polyenoic acids indicates whether they have an all-*cis*-, an all-*trans*-, or a *cis-trans*-configuration.

The relative proportions of *cis*- and *trans*-ethylenic bonds in conjugated polyenoic acids can be determined by measuring the intensity of the band in the range 970–1000 cm^{-1}, which is characteristic of non-planar deformation vibrations of *trans*-hydrogen atoms adjacent to double bonds. This parameter was found to be directly proportional to the number of *trans*-ethylenic bonds in a polyene chain, and is a multiple of the intensity of the corresponding band (968 cm^{-1}) in the spectrum of elaidic acid (provided that measurements are made on the same instrument)[11] (Table 3).

TABLE 2. Characteristic frequencies of infrared absorption bands due to ethylenic bonds in isomeric nona-2,4-dienols and methyl deca-2,4-dienoates.[2]

Configuration of 2,4-diene system	2,4-Dienols			Methyl deca-2,4-dienoates		
	stretching vibrations		deformation vibrations	stretching vibrations		deformation vibrations
	C=C (1)	C=C (2)	(CH=CH)$_2$	C=C (1)	C=C (2)	(CH=CH)$_2$
trans-trans	1660	1626	986, —	1647	1618	1001, —
trans-cis	1655	1616	983, 948	1639	1607	996, 969
cis-trans	1652	1609	984, 952	1640	1602	1002, 963
cis-cis	1651	1601	985*, 951*	1634	1592	1002*, 963*

* The presence of these bands is explained by contamination with *trans*-isomers owing to the ready isomerisation of the *cis-cis*-form.

TABLE 3. Extinction coefficients K of C_{18} aliphatic acids $CH_3[CH_2]_n[CH{:}CH]_m[CH_2]_kCOOH$ in the range 900–1000 cm^{-1} of the infrared spectra.[11]

n	m	k	Configuration	ν_{max}, cm^{-1}	K
7	1	7	*cis*	968	0.124
7	1	7	*trans*	968	0.601
5	2	7	*trans-trans*	987	1.270
5	2	7	*cis-trans*	950	0.501
				985	0.453
4	2	8	*trans-trans*	987	1.250
4	2	8	*cis-trans*	950	0.565
				985	0.485
3	3	7	*trans-trans-trans*	994	1.955
3	3	7	*cis-trans-trans*	965	0.416
				992	1.425
1	4	7	all-*trans*	998	2.80
1	4	7	2-*cis* and 2-*trans*	952	0.483
				994	1.55

Besides physicochemical methods for investigating the structure of conjugated polyenoic acids, use is made also of such classical chemical methods as catalytic hydrogenation, halogenation, and oxidative cleavage. The last of these methods (ozonolysis and the permanganate–periodate method) enables the position of a polyene group in an aliphatic chain to be determined, since it involves formation of monocarboxylic and dicarboxylic acids each containing one extra carbon atom compared with the radicals attached to the double bonds:

$$RCH{=}CH{-}CH{=}CH[CH_2]_nCOOH \xrightarrow{[O]} RCOOH + HOOC[CH_2]_nCOOH.$$

The above methods make it possible to establish the structure of the acids and to determine the ratio of *cis*- and *trans*-ethylenic bonds. However, the sequence of the double bonds cannot be determined by these methods. In most cases this question can be answered by studying the products of the diene condensation of the polyenoic acids with maleic anhydride. Among conjugated dienes, it is usually only aliphatic *trans-trans*-dienes which undergo the Diels–Alder reaction. The *cis-trans*-dienes either do not react at all with maleic anhydride or else react under severe conditions in a manner differing from that of diene synthesis[14,15]. The formation of adducts with maleic anhydride may serve as evidence of the presence of a conjugated *trans-trans*-diene group in a polyene compound, and has been used in establishing the configuration of naturally occurring conjugated trienoic acids. In this case the configuration of the third ethylenic bond in the acid, which remains unchanged in the aliphatic chain of the adduct, can be confirmed by infrared spectroscopy: the methyl esters of adducts containing an exocyclic *trans*-ethylenic bond exhibit an intense band in the range 1000–950 cm^{-1}, whereas this band is absent with adducts containing a *cis*-bond[16,17].

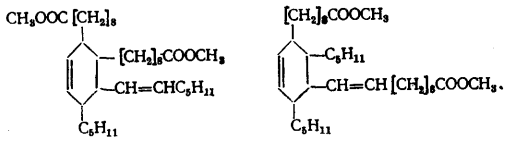
All natural polyenoic acids containing conjugated bonds are distinguished by considerable instability. They are extremely readily oxidised in the air, to form various hydroperoxides, which in turn initiate polymerisation processes[18]. Acids containing one or more *cis*-ethylenic bonds are oxidised considerably more readily than are all-*trans*-isomers[19] (see Table 4).

TABLE 4. Rate of oxidation of octadecatrienoic acids at 40°.[20]

Acid	Configuration of unsaturated system	Molar O_2/acid ratio after 100 min
α-Elaeostearic	*cis-trans-trans*, conjugated	2.68
β-Elaeostearic	*trans-trans-trans*, conjugated	1.02
Linolenic	*cis-cis-cis*, unconjugated	0.52

The presence of traces of water, irradiation, heating, and other factors considerably accelerate the polymerisation of these compounds[18,21]. These facts are of fundamental importance in the application of derivatives of polyenoic acids in the manufacture of varnishes.

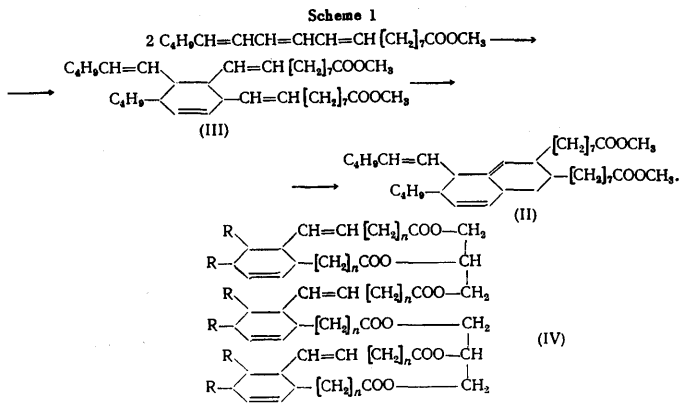
The thermal polymerisation (in the absence of oxygen) of compounds containing different numbers of double bonds, of different degrees of conjugation, and differing in configuration also occurs at different rates. Thus the thermal polymerisation of conjugated *trans-trans*- and *trans-cis*- and of unconjugated *cis-cis*-dienoic C_{18} acids takes place at relative rates of 40 : 7 : 1.[21] Their polymerisation probably has a bimolecular mechanism of diene condensation[22], but intramolecular cyclic structures may be formed. It has been discovered that unconjugated and conjugated dienoic acids give identical dimerisation products, which indicates that the polymerisation of unconjugated polyenoic acids involves their conversion into conjugated acids[22]. The most detailed investigation that has now been made is of the structure of the products formed by the polymerisation of methyl octadeca-*trans*-10, *trans*-12-dienoate, which are obtained when it is heated at 250° for 5 h. The results of nuclear magnetic resonance, mass, and infrared spectroscopy and of ozonolysis have shown that the main products of this reaction are 3,4,5,6-tetrasubstituted cyclohexene dimers of type (I), having an αβ-ethylenic bond in a side-chain[23].



(Ia) (Ib)

Under these conditions trienoic esters probably form dicyclic dimers of type (II) or monocyclic dimers having the structure (III) (see Scheme 1)[22,24], whereas their triglycerides yield structures of type (IV). The dimeric molecules may undergo further condensation by interaction at isolated double bonds with the conjugated bonds of the monomers[25].

Scheme 1



3. DIENOIC ACIDS

Stillingic Acid

The only C_{10} dienoic acid which has been found in Nature is deca-2,4-dienoic (stillingic) acid, which has been isolated from the seed oil of *Sapium sebiferum* (the Chinese tallow tree) and *S. discolor*. The content of stillingic acid in the oils of these seeds does not exceed 4–5%. A 2,4-dienoic acid was first detected in these sources from the characteristic absorption maximum in the ultraviolet spectrum (260 nm);[26,27] soon after this it was isolated and characterised, and its structure was established[28-31].

Stillingic acid oxidises in the air even at ordinary temperatures. Exhaustive hydrogenation yields n-decanoic acid. The products of destructive oxidation of its methyl ester are found to include n-hexanoic acid, the formation of which proves that the ethylenic bonds in the dienoic acid are located in the 2- and 4-positions[28]. Partial hydrogenation of methyl stillingate gave mainly the dec-3-enoic ester, together with small quantities of the dec-2-enoate and dec-4-enoate. Reduction of methyl stillingate with lithium tetrahydroaluminate gave deca-2,4-dienol, which had an ultraviolet absorption maximum at 231 nm (ε = 22 500), and on alkaline isomerisation a mixture of deca-4,6- and -5,7-dienoic acids was formed[31].

Since the configuration of the diene system of stillingic acid could not be established in the original investigation[28-31], nor could it be satisfactorily analysed or its crystalline derivatives characterised, a further detailed study was made of this acid[2]. In order to establish its configuration, all four possible geometric isomers of deca-2,4-dienoic acid were synthesised (see Section 5). The naturally occurring acid and the synthetic *trans*-2,*cis*-4-isomer had the same ultraviolet and infrared spectra and gave identical *p*-bromophenacyl esters and *S*-benzylthiouronium salts, so that the *trans*-2,*cis*-4-configuration was proposed for stillingic acid.

Dodeca-2,4-dienoic Acid

A dodeca-2,4-dienoic acid has been detected in the seed oil from *Sebastiana lingustrina* (Euphorbiaceae family), a plant growing in North America[32]. Two moles of hydrogen are absorbed on hydrogenation, with the formation of lauric acid. The position of the absorption maximum in the ultraviolet spectra of the methyl ester (268 nm) and of the acid (260 nm, ε = 33 400) is characteristic of 2,4-dienoic acids[2,33]. The configuration of the diene grouping in this acid has not yet been settled. From the position of the ultraviolet absorption maximum for methyl dodeca-2,4-dienoate, the acid may be supposed to be the *trans*-2,*cis*-4-isomer, but the position of the maximum in the ultraviolet spectrum of the acid itself and the extinction are characteristic of acids having a *trans-trans*-configuration.

Octadeca-*trans*-10,*trans*-12-dienoic Acid

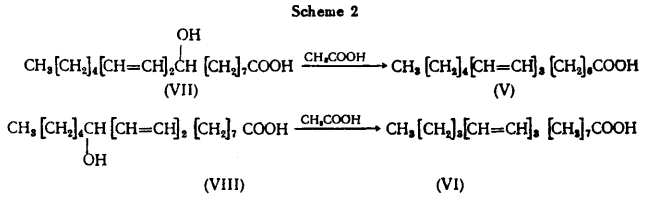
A positional isomer of this acid having an unconjugated system of double bonds — linoleic acid — is the most widespread "essential" fatty acid in Nature. In spite of this, no isomer of it having conjugated bonds was known until recently. There were only isolated references to the presence of such an isomer in lipids from the plant *Catalpa bignonioides* and *Chilopsis linearis*[5,8,34] and in some other

plants[35,36]. The seeds of *Chilopsis linearis*, a small ornamental tree from the Southern USA, contain a trienoic as well as the dienoic acid. Careful low-temperature recrystallisation of the mixture of these acids obtained by saponifying the seed oil resulted in the isolation of 9% of a dienoic acid having m.p. = 55–56° and λ_{max} = 232 nm (ϵ = 29 200), with infrared absorption bands at 985 and 930 cm^{-1}.[37] Catalytic hydrogenation of this acid yielded strearic acid. The location of the diene grouping at the 10,12-positions was proved by oxidative cleavage. Although only one intense absorption band is usually oserved in the range 900–1000 cm^{-1} in the infrared spectra of conjugated *trans*-*trans*-dienes, this configuration was assigned to the octadeca-10,12-dienoic acid which was isolated, since the latter formed an adduct with maleic anhydride (m.p. 102–103°) which gave no melting-point depression on fusion with a known specimen[38]. This acid had been obtained previously by the dehydration and isomerisation of ricinoleic acid isolated from castor oil[39], and by the alkaline isomerisation of linoleic acid[1].

cis-trans-9-Hydroxyoctadeca-10,12-dienoic and -13-Hydroxyoctadeca-9,11-dienoic Acids

The oil from the plants *Tragopogon porrifolius* (Compositae family) is known as a source of saturated epoxy-acids[40]. It has recently been found to contain a polyene fraction of unusual composition, in amount not exceeding 4–5% according to ultraviolet spectral data[7]. After separation of unsaponifiable products, conjugated dienoic acids having an ultraviolet absorption maximum at 233 nm and infrared absorption bands at 3580, 945, and 980 cm^{-1} were isolated. The first band indicated the presence of a hydroxyl, and the latter bands the presence of a *cis-trans*-diene grouping. The mixture of dienoic acids isolated was subjected to oxidative cleavage by the permanganate–periodate method, which showed the presence of diene groupings in the 9,11- and 10,12-positions. On boiling with glacial acetic acid the mixture of acids formed a mixture of octadeca-8,10,12- and -9,11,13-trienoic acids — (V) and (VI), see Scheme 2.

Scheme 2



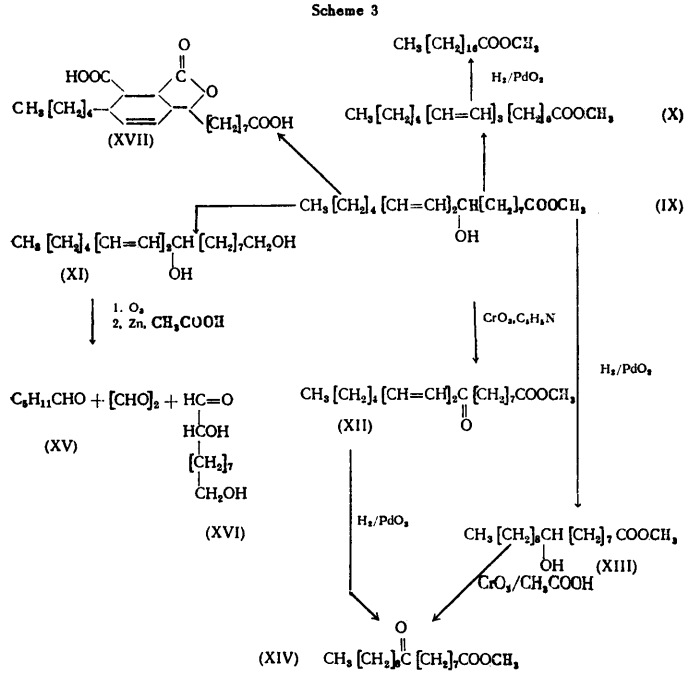
Catalytic hydrogenation of this mixture of trienoic acids yielded stearic acid, whereas oxidative cleavage yielded valeric, suberic, and azelaic acids. The ease of dehydration indicated that the hydroxy-groups in the original acids occupied an allylic position with respect to the diene grouping. This suggestion was confirmed by study of the hydrogenation products obtained from the mixture of hydroxy-acids (VII) and (VIII), which comprised a mixture of monohydroxystearic acids of m.p. 65–66°. The location of the hydroxyls in the latter acids (at positions 9 and 13) was proved by oxidative cleavage to the corresponding dicarboxylic and monocarboxylic acids.

On the basis of the infrared spectra of the natural acids and their esters, a *cis-trans*-configuration was assigned to them. However, spectral data do not permit the possibility to be excluded that only one of the dienoic acids may possess a *cis-trans*-configuration, while the other may have a *cis*-*cis*- or *trans*-*trans*-configuration. The position of the *cis*- and *trans*-ethylenic bonds in the molecules of the natural acids remains undetermined.

Dimorphecolic Acid

In order to find new sources for valuable industrial oils, a study was made of the composition of lipids from a large group of plants of the Compositae family[41]. Several of them, in particular the oil from *Dimorphotheca aurantiaca* (or *D. sinuata*), were found to contain a considerable quantity (up to 50%) of a conjugated dienoic acid as well as epoxy-acids. Mild saponification of this oil gave a dienoic acid, sensitive to alkali under more severe conditions, which was purified by countercurrent distribution as the methyl ester in an acetonitrile–hexane system. The methyl ester (IX) exhibited optical activity, absorbed in the ultraviolet at 231 nm, and possessed infrared absorption bands corresponding to a conjugated *trans*-*trans*-diene (992 cm^{-1}) and a hydroxy-group. On boiling under conditions of acetolysis of the epoxy-compounds, the dimorphecolic ester was converted into a trienoic acid (X) containing no hydroxyl, which was reduced catalytically to stearic acid. Lithium tetrahydroaluminate reduction of the ester (IX) to the dienediol (XI) also confirmed the absence of an epoxy-group in the ester molecule (IX). Oxidation with chromium trioxide yielded the dienone (XII), which had a maximum in the ultraviolet spectrum at 275 nm, corresponding to $\alpha\beta$- and $\gamma\delta$-unsaturated ketones. The location of the hydroxyl in dimorphecolic acid was established by comparing the products obtained by reducing the keto-ester (XII) and oxidising the hydroxy-ester (XIII) with the identical synthetic keto-ester (XIV). Furthermore, ozonolysis of the dienediol (XI) yielded glyoxal and the aldehydes (XV) and (XVI), identified as their 2,4-dinitrophenylhydrazones. On the other hand, dimorphecolic ester (IX) reacts with maleic anhydride to form a lactone (XVII), which confirms the *trans*-*trans*-configuration of the 10,12-diene grouping in dimorphecolic acid[42] (see Scheme 3).

Scheme 3



Methods were later developed, to meet the requirements of the paint and varnish industry, for isolating dimorphecolic acid as its methyl ester from the triglycerides in *Dimorphotheca* oil, these involving transesterification of the oils in methanolic solution on a hydroxylated ion-exchange resin [43,44].

Dimorphecolic acid has subsequently been found in the oils from 29 species of plants, in which it constitutes 34–75% of the total acids [45]. There is indirect evidence of the presence in some of these specimens of another isomer of dimorphecolic acid, with the hydroxyl in position 13 and the diene grouping in positions 8 and 10. [46]

The ready dehydration of dimorphecolic acid makes it a very probable biological precursor of calendic acid (see below), which was found to accompany the former in most of the plants investigated [45].

TABLE 5. Natural sources of α-elaeostearic acid.

Plant	% of total acids	Ref.
Aleurites cordata	74	50
» *fordii*	77—86	51—53
» *montana*	71—82	54
» *trisperma*	51—67	55,56
Garcia nutans	93—95	57,58
Licania rigida	16—17	59
Mallotus phillipinensis	38	60
Parinarium campestre	49	61
» *corymbosum*	13—15	61
» *laurinum*	30—34	62
» *macrophyllum*	30—32	53,63,64
» *scherbroense*	32—37	65
Ricinodendron africanum	49—53	66
Telfaira occidentalis	19	67
Catalpa bignonioides	31	68
Momordica charantia	57	69—71

4. TRIENOIC AND TETRAENOIC ACIDS

Since trienoic acids may differ from one another both in the position of the triene system in the aliphatic chain and in the configuration of the double bonds, the number of possible isomers is very large. In spite of this, only eight naturally occurring acids of this type are known at the present time. They all oxidise and polymerise readily in air even at room temperature.

α-Elaeostearic Acid

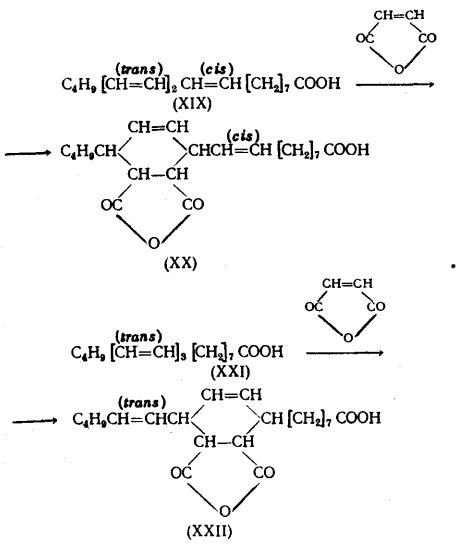
α-Elaeostearic acid is the most widely occurring conjugated trienoic acid in Nature (Table 5). The best-known source of the acid is tung oil, from which it was isolated as long ago as 1875. [47,48] The formula $C_{18}H_{30}O_2$ was established for α-elaeostearic acid in 1902, and a higher-melting β-form was obtained for the first time [49]. Pure α-elaeostearic acid, isolated from tung oil and purified by low-temperature recrystallisation from alcohol, melts at 48°. [3,4] Under the influence of ultraviolet radiation in the presence of traces of iodine or sulphur, it is readily converted into β-elaeostearic acid melting at 72°. [4] Both acids form adducts with maleic anhydride on heating in benzene, these melting at 62.5° and 77° respectively [72], and bromination yields hexabromides melting at 139–141° and 157°. [73,74] α-Elaeostearic acid forms a crystalline *p*-phenylphenacyl ester melting at 63–64°. [70] On catalytic hydrogenation both acids give stearic acid, equimolecular mixtures of isomeric octadecenoic acids being formed as intermediate products [75–77]. The action of hydrazine on α- and β-elaeostearic acids involves reduction firstly of terminal units in the polyene chain, with the formation of the 11-enoic and the 9,11- or 11,13-dienoic acids, a *cis*--ethylenic bond in the polyene system being reduced rather more rapidly [78] [than the corresponding *trans*-bond (Ed. of Translation)].

The ultraviolet spectra of α- and β-elaeostearic acids show absorption maxima characteristic of trienes — at 261, 271, and 281 nm (ε = 36 000, 47 000, and 38 000 respectively); and at 259, 268, and 279 nm (47 000, 61 000, and 49 000). [3]

At 0° both forms add on two molecules of bromine to form tetrabromides, so for a long time they were regarded as dienoic acids, to which different cyclic structures were attributed. It was later suggested that the ethylenic bonds in the acids were conjugated [79], and valeraldehyde, valeric acid, and azelaic acid were detected in the hydrolysis products of their ozonides [80]. Together with the facts that on catalytic hydrogenation 1 mole of elaeostearic acid absorbed 3 moles of hydrogen and that its molecular refraction was too high to correspond to a diene, this enabled the true structure of the acid to be established [81,82]. The structure of elaeostearic acid was confirmed also by the 60% yield of glyoxal obtained on hydrolysis of its ozonide, while no succinic or malonic acid was detected [83]. Hexabromostearic acid was subsequently obtained [73,74] by bromination with ultraviolet irradiation and heating. Thus the structural formula of elaeostearic acid was finally established by 1930, but its configuration remained unelucidated.

The original investigations of the structure of the adducts formed by α- and β-elaeostearic acids with maleic anhydride did not provide the right answer to this question [72,81–87]. The location of the cyclohexene ring in the aliphatic chain of the adducts was merely established, and an adduct having the structure (XX) was shown to be formed from α-elaeostearic acid (XIX), since azelaic acid was detected among the products of the oxidative cleavage of this adduct (Scheme 4).

Scheme 4



The structure of the adduct formed by maleic anhydride with β-elaeostearic acid was established (XXII) in a similar manner[72].

After it had been ascertained that maleic anhydride undergoes diene condensation only with *trans-trans*-diene groups[14], several authors suggested that α-elaeostearic acid had the *cis*-9,*trans*-11,*trans*-13-configuration (XIX), while β-elaeostearic acid was the all-*trans*-isomer (XXI).[11,16,17,88] These configurations were subsequently confirmed by examination of the infrared spectra. Thus α-elaeostearic acid (XIX) exhibits intense absorption bands in the region of out-of-plane deformation vibrations of *trans*-ethylenic hydrogen atoms at 992 and 965 cm^{-1}, with intensity coefficients K of 1.43 and 0.416 respectively; the infrared spectrum of the β-isomer (XXI) has an absorption band at 994 cm^{-1} with K = 1.96, threefold the intensity of the corresponding band for elaidic acid at 968 cm^{-1}. From this it was concluded that the β-isomer had an all-*trans*-configuration. From the same considerations the α-acid (XIX) was assumed to contain one *cis*-ethylenic bond[11]. In this case one of three configurations — *trans-trans-cis*, *cis-trans-trans*, or *trans-cis-trans* — was possible, of which the second was the most probable, since α-elaeostearic acid formed only an adduct having the structure (XX). Furthermore, the infrared spectrum of the methyl ester of the adduct (XXII), in contrast to the adduct (XX), contained an absorption band in the range 1000–950 cm^{-1}, indicating that the ethylenic bond in the aliphatic chain of the adduct (XXII) had the *trans*-configuration[16,17].

The structure (XIX) for α-elaeostearic acid was finally proved by synthesis (see Section 5).[4,89]

Punicic Acid

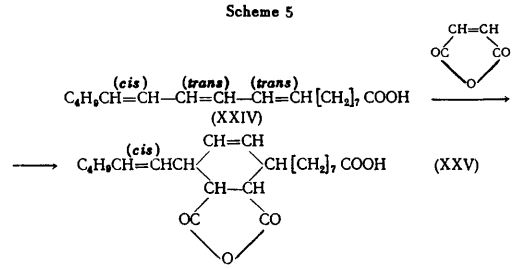
Punicic acid was first isolated from the seed oil of the pomegranate (*Punica granatum*)[90], where it forms 72% of the total aliphatic acids. It is met also in the plants *Momordica balsamina*[72], *Trichosanthes anguina* (43%)[70], *Ecballium elaterum* (Cucurbitaceae) (22%)[71], etc. The ultraviolet spectrum of punicic acid (m.p. = 42°) contains three maxima, at 265.5, 275 (ε = 47 800), and 287 nm. The infrared spectrum contains absorption bands at 988 and 937 cm^{-1} (K = 0.63 and 0.7 respectively)[91]. On the basis of these data it was suggested — erroneously, as appeared later — that punicic acid had a *cis-cis-trans*-configuration[91,92]. The acid does not form an adduct with maleic anhydride, and on ultraviolet irradiation is converted into β-elaeostearic acid (XXI).[16]

At roughly the same time an acid melting at 35–35.5°, which was termed "trichosanic acid", was isolated from the oil of the Japanese snake gourd (*Trichosanthes cucumeroides*)[90]. Its ultraviolet and infrared spectra were identical with those of punicic acid, and under the influence of ultraviolet radiation both acids isomerised into β-elaeostearic acid (XXI), so that trichosanic acid was assumed to be a third geometric isomer of α-elaeostearic acid (XIX). The presence of trichosanic acid in Japanese snake gourd[93,94], and also in the oil of the Indian snake gourd (*Trichosanthes anguina*)[94,95], was subsequently confirmed by other workers. In order finally to establish the structure of punicic and trichosanic acids, the synthesis was then undertaken of two isomeric octadecatrienoic acids by Scheme 10*b*. Comparison of natural and synthetic specimens showed that both punicic and trichosanic acids were octadeca-*cis*-9,*trans*-11,*cis*-13-trienoic acid (XXIII).

Catalpic Acid

Catalpic acid was isolated from the seed oil of the decorative plant *Catalpa ovata* (Bignoniaceae)[8], *C. speciosa*[71], and *Chilopsis linearis*[37,38]. α-Elaeostearic acid (XIX) had previously been found in the seed oil of various *Catalpa* species[68]. Pure catalpic acid was still less stable than punicic acid (XXIII) or α-elaeostearic acid. It melts at 31–32°, and oxidised rapidly in the air, being converted into a non-crystalline solid mass even at room temperature. Its ultraviolet spectrum contains absorption maxima at 262, 272 (ε = 49 300), and 283 nm, which are characteristic of conjugated trienes[8]. The character of these maxima, together with the results of elementary analysis and hydrogenation, showed that catalpic acid, like elaeostearic and punicic acids, is an octadecatrienoic acid containing a conjugated system of ethylenic bonds.

Scheme 5



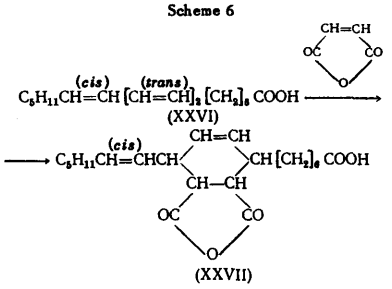
Gas–liquid chromatography of the products obtained by the oxidative cleavage of catalpic acid has shown that the triene grouping occupies the 9–13 positions. This is confirmed also by the isomerisation of catalpic acid (XXIV) into β-elaeostearic acid (XXI) on ultraviolet irradiation in the presence of iodine. The infrared spectrum of catalpic acid (XXIV) resembles that of α-elaeostearic acid, containing in particular bands at 987 and 957 cm^{-1} of the same relative intensities as with the latter acid. Catalpic acid (XXIV) readily forms an adduct (XXV) with maleic anhydride (Scheme 5), melting at 72.5–73.5° and possessing no infrared absorption band in the range 950–1000 cm^{-1}, so that the double bond in the aliphatic chain of the adduct has the *cis*-configuration. Of the eight possible isomers of octadeca-9,11,13-trienoic acid, only two — the *trans-trans-cis*- and *cis-trans-trans*-isomers — are able to form such an adduct. Since the latter isomer is α-elaeostearic acid (XIX), only the structure (XXIV) is available for catalpic acid. A complete synthesis of catalpic acid has recently been achieved by means of the Wittig reaction (Scheme 13).

Calendic Acid

Calendic acid has been isolated from the seed oil of *Calendula officinalis* (Compositae)[5]. Its isomer having the *trans-trans-trans*-configuration (β-calendic acid) is not present in this oil, but is obtained from it as a result of the isomerisation of calendic acid in the course of isolation[7]. Conjugated trienoic acids, in particular octadeca-8,10,12-trienoic acid, have been detected in other plants — *Calendula arvensis*, *Osteospermum*, *Chrysanthemoides* — which are closely related to *Calendula*[45,96]. Calendic acid (XXVI) (m.p. 40–40.5°) was purified by low-temperature recrystallisation from acetone, and elementary analysis showed it to be an octadecatrienoic acid. On catalytic hydrogenation, α-calendic acid absorbs three molecules of hydrogen to form stearic acid. Oxidative cleavage of calendic acid results in rupture of the bonds in the positions 8–13. The

infrared spectrum of calendic acid contains absorption bands at 990 and 955 cm^{-1}, which suggests the presence of conjugated *cis*- and *trans*-ethylenic bonds. A similar conclusion follows also from an examination of the positions of its ultraviolet absorption maxima (at 262, 272, and 283 nm). Calendic acid reacts readily with maleic anhydride (Scheme 6) to form an adduct of m.p. 73–74°, whose infrared spectrum does not contain the absorption bands in the range 1000–950 cm^{-1} which are characteristic of the spectra of adducts containing an exocyclic *trans*-ethylenic bond. Oxidative cleavage of the adduct by the permanganate–periodate method yields only one monocarboxylic acid — n-hexanoic acid — so that the adduct has the formula (XXVII). Thus the *trans*-8,*trans*-10,-*cis*-12-configuration has been established for calendic acid.

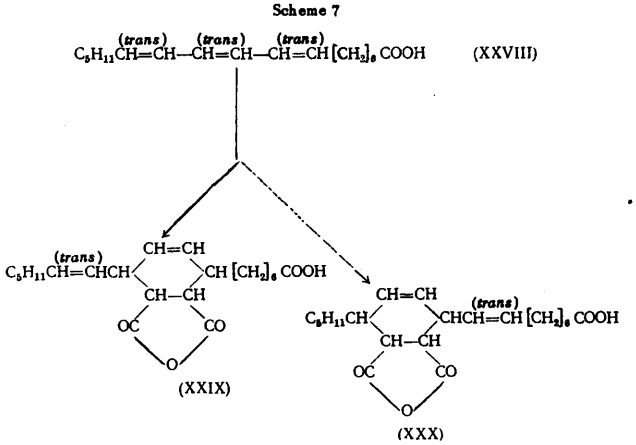
Scheme 6



(XXVII)

When calendic acid is treated with iodine in pentane and on ultraviolet irradiation, it passes into β-calendic acid (XXVIII), melting at 77–78° and exhibiting an intense infrared peak at 990 cm^{-1}.[11,17] A 950 cm^{-1} band is also present in the infrared spectrum of the photochemical isomerisation product, but its intensity is considerably less than in the infrared spectrum of the original *trans-trans-cis*-isomer (XXVI). The ultraviolet absorption maxima of β-calendic acid (XXVIII) are displaced to shorter wavelengths in comparison with natural calendic acid (XXVI) (258, 268, and 280 nm compared with 262, 272, and 283 nm)[7] (see Scheme 7). The infrared spectrum of the adduct formed by β-calendic acid with maleic anhydride (m.p. 70–71°) contains an absorption band at 963 cm^{-1}, which is characteristic of a *trans*--exocyclic double bond. Permanganate–periodate cleavage of this adduct gave both n-hexanoic and suberic acids, so that the adduct melting at 70–71° was a mixture of the isomers (XXIX) and (XXX). Further confirmation of the structure of calendic acid has been provided by its complete synthesis (Scheme 13).

Scheme 7



(XXIX) (XXX)

Jacarandic Acid

Another stereoisomer of calendic acid (XXVI) — jacarandic acid (XXXI), found in the seed oils of *Jacaranda mimosifolia* (Bignoniaceae) and *Dimorphotheca aurantiaca*[5,58] — is stereochemically analogous to punicic acid (XXIII). These two acids are very similar in spectral characteristics and in melting points (43.5–44°).

Jacarandic acid oxidises very readily in the air, and is extremely unstable at temperatures above -20°. Catalytic hydrogenation and oxidative cleavage have shown it to be a C_{18} acid having a triene grouping in the positions 8–12 of the aliphatic chain[5,31]. Furthermore, this acid does not form an adduct with maleic anhydride, and on ultraviolet irradiation passes into a higher-melting form which proves to be identical with β-calendic acid (XXVIII). All these results indicate the absence of a *trans-trans*-diene grouping and the presence of at least one *cis*-ethylenic bond in jacarandic acid. Structures containing *cis-trans-trans*-, *trans-trans-cis*-, or *trans-trans-trans*-triene systems are therefore excluded. The presence in the infrared spectrum of jacarandic acid of an intense band at 982 cm^{-1} (together with a band at 929 cm^{-1}), which is characteristic of a *trans*-ethylenic bond, also excludes a *cis-cis-cis*--configuration. The *cis-cis-trans*- and *trans-cis-cis*--structures were rejected on the grounds that the infrared and ultraviolet spectra of jacarandic acid (XXXI) and of synthetic octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid[4] differ fundamentally. In particular, the ultraviolet spectrum of the synthetic acid contains only one absorption maximum, at 271 nm, with inflections at 263 and 279 nm, whereas the spectrum of jacarandic acid is characterised by a triplet at 265, 275, and 287 nm. Of the two possible remaining structures — *cis-trans-cis* and *trans-cis*--*trans* — the latter is inconsistent with the fact that the intensity of the absorption band at 982 cm^{-1} in the infrared spectrum of jacarandic acid is close to the intensity of the corresponding band of elaidic acid.

$$C_5H_{11}\overset{(cis)}{C}H{=}\overset{(trans)}{C}H{-}\overset{(trans)}{C}H{=}\overset{(cis)}{C}H{-}CH{=}CH[CH_2]_6COOH \quad (XXXI).$$

On the basis of all the above results, the structure (XXXI) has been put forward for jacarandic acid.

Kamlolenic Acid

Kamlolenic acid is the main aliphatic acid in the oil from the kernels of *Mallotus philippinensis* (Euphorbiaceae), which has long been used as a purgative in popular medicine[97–100]. Like other trienoic acids, kamlolenic acid is known in the form of two geometric isomers[101]: the natural α-form melts at 77–78°; the β-isomer, formed from the α-form on ultraviolet irradiation, melts at 88–89°. Both forms yield crystalline methyl and *p*-bromophenacyl esters, acetyl derivatives, and 1-naphthylurethanes of the methyl esters[98,102]. On catalytic reduction both forms absorb three moles of hydrogen with the formation of 18-hydroxystearic acid[97–99,102]. The infrared spectra of the stereoisomeric kamlolenic acids and their methyl esters contain intense absorption bands at 3200 and 1060 cm^{-1}, due to a primary hydroxyl, while the spectrum of the α-isomer includes an intense doublet in the range 900–1000 cm^{-1}.[102]

Ozonolysis of methyl kamlolenate yielded the 9-oxononanoic ester, formed by cleavage of a 9,10-ethylenic bond[102]. Study of the infrared spectra of both isomeric forms, their acetyl derivatives, and the maleic anhydride

adducts led to the proposed structures (XXXII) for the α-form and (XXXIII) for the β-form [103-105].

$$HO[CH_2]_4\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(cis)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(cis)}{CH}{=}CH[CH_2]_7COOH \quad (XXXII)$$

$$HO[CH_2]_4\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(trans)}{CH}{=}CH[CH_2]_7COOH. \quad (XXXIII)$$

These structures have also been confirmed by the complete synthesis of α-kamlolenic acid by Scheme 15. The earlier suggestion that this compound was an unsaturated keto-acid [100] proved to be erroneous.

Licanic Acid

Licanic acid was first isolated in 1931, from the seed oil of the tropical tree *Licania rigida* [106]. In one of the early papers [107] the source of this acid was erroneously included in the family Couepia (*C. grandiflora*), on which basis it was given a different name, "couepic acid". Licanic acid was subsequently isolated also from other *Licania* species — *L. arbrorea* (*cacahunanche*) (Mexico) [108], *L. crassifolia* (East Indies) [109], *L. levenosa* (British Guiana) [110] — in the oils from which the content of this acid reaches 80% of the total acids. Furthermore, it accompanies eleaeostearic acid to form 35–70% of the seed oils from certain plants of the genus *Parinarium*, in particular *P. corymbosum* (*taritih*) [111], *P. glaberimum* (India) [19], *P. laurinum* (*makita*) (islands in the Pacific Ocean) [19], *P. macrophyllum* (*neou*) [62-64], and *P. sherbroense* (Africa) [65].

$$C_4H_9\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(trans)}{CH}{=}\overset{(cis)}{CH}{-}\overset{(cis)}{CH}{=}CH[CH_2]_4CO[CH_2]_2COOH \quad (XXXIV)$$

$$C_4H_9\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(trans)}{CH}{=}\overset{(trans)}{CH}{-}\overset{(trans)}{CH}{=}CH[CH_2]_4CO[CH_2]_3COOH \quad (XXXV)$$

Licanic acid melts at 63°. It forms a semicarbazone (m.p. 134–137° [112,113]) and an adduct with maleic anhydride (m.p. 79° [114]). Photochemical isomerisation of the natural α-licanic acid yields the higher-melting β-form (isolicanic acid, m.p. 99.5°). [16] Ultraviolet spectroscopy indicates that licanic acid contains a conjugated triene grouping. On catalytic reduction (after the absorption of three moles of hydrogen) 4-oxostearic acid is formed, and oxidation with dilute potassium permanganate solution at 0° yields n-valeric, 4-oxoazelaic, and oxalic acids. With maleic anhydride α-licanic acid forms an addition product in the 11,14-positions, since ozonolysis of the adduct yielded 4-oxoazelaic acid, while valeric acid was also detected in the case of β-licanic acid. On the basis of these results, and also the infrared spectra of α- and β-licanic acids and their adducts, the structures (XXXIV) and (XXXV) were suggested for these acids [16].

5-Acetoxymethyltetradeca-*trans*-2,*trans*-4,*trans*-6-trienoic Acid

Resinous substances in the leaves of the Australian tree *Eremophila oppositifolia* (Myoporaceae) contain, together with a large quantity of sesquiterpene alcohols, an unsaturated acetoxy-acid of m.p. 88–89° and empirical formula $C_{17}H_{26}O_4$. [115] The infrared spectrum of this acid contains bands corresponding to a conjugated triene grouping (980 and 965 cm^{-1}), an ester group (1743 cm^{-1}), and a carbonyl group (1686 cm^{-1}). Its ultraviolet spectrum contains a single maximum at 298 nm, characteristic of a triene system conjugated with a carboxyl.

On saponification of the acid (XXXVI) an intense band appears in the infrared spectrum at 3621 cm^{-1}, corresponding to an alcoholic hydroxyl. Catalytic reduction of the unsaturated acetoxy-acid (XXXVI) yields a mixture of 5-methyltetradecanoic acid (XXXVII) (hydrogenolysis product) and the saturated acetoxy-acid (XXXVIII) (see Scheme 8). The hydroxy-acid (XXXIX), obtained together with acetic acid on saponification of the natural acetoxy-acid (XXXVI), can be oxidised with manganese dioxide to the aldo-acid (XL), which indicates that its alcoholic hydroxyl occupies an allylic position [116]. The hydroxy-acid (XLI) is oxidised by chromic acid to a dicarboxylic acid (XLII), which on being heated with acetic anhydride yields 2-nonylcyclopentanone (XLIII), the formation of which proves that the side-chain in the natural acid (XXXVI) is attached to the $C_{(5)}$ atom.

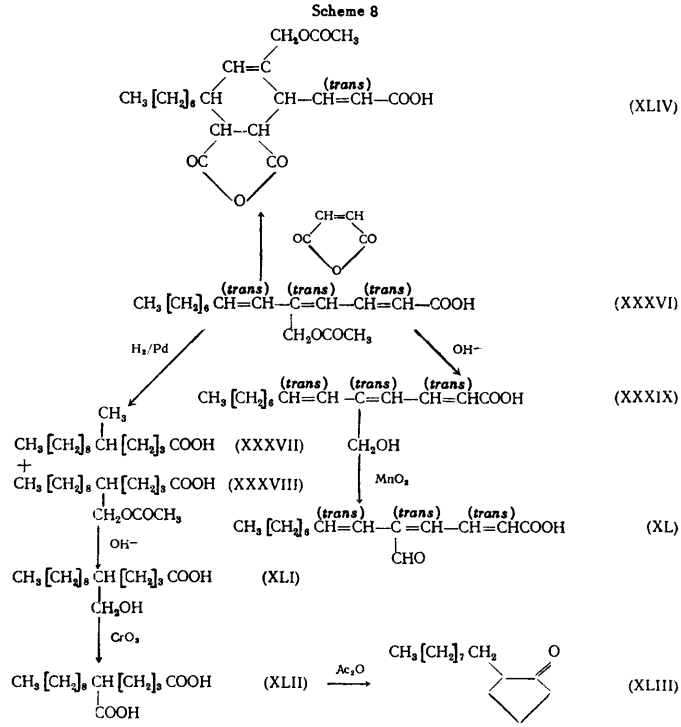
The position of the triene grouping in the aliphatic chain of the natural acid (XXXVI) was established by ozonolysis (n-octanal was found among the reaction products). This acid interacts with maleic anhydride to form an adduct (XLIV), whose infrared spectrum contains an absorption band at 965 cm^{-1}, which indicates that the exocyclic ethylenic bond in the adduct has the *trans*-configuration [16,17].

On the basis of these results the structure 5-acetoxymethyltetradeca-*trans*-2,*trans*-4,*trans*-6-trienoic acid (XXXVI) has been proposed for the naturally occurring acid.

Tetraenoic (Parinaric) Acids

Parinaric acid (XLV), first isolated from the oil obtained from *Parinarium laurinum* nuts (Table 6), was originally regarded as a trienoic acid, isomeric with elaeostearic acid (XIX). [117,119] Subsequently catalytic hydrogenation and determination of the iodine number established that four ethylenic bonds were present, and they were proved by ultraviolet

Scheme 8



(XLIV)

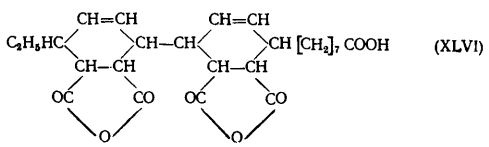
TABLE 6. Natural lipids containing parinaric acids.

Plant	Content in acid mixture, %	Ref.
Parinarium laurinum	46—56	117,118
Impatiens balsamina	—	121
» *fulva*	51	122
» *parviflora*	46	123,124
» *Royley*	40—50	122
» *holimetangre*	32	122
» *hortensis*	27	122
» *Sultanii*	—	122
» *Holstii*	13	122
Nyphaea alba	—	123
» *Iris*	—	123

spectroscopy [119,120] and oxidative cleavage [119] to be conjugated. Since propionic and azelaic acids were detected among the products of ozonolysis, the tetraene grouping in parinaric acid should occupy the positions 9–15 [118] (XLV).

Natural parinaric acid (the α-form), melting at 84–85°, can be converted by photochemical isomerisation into the β-form, having m.p. 95–96°, which was assigned the all-*trans*-configuration on the grounds that it formed an adduct with two molecules of maleic anhydride (XLVI). [124]

$$C_5H_9CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH\,[CH_2]_7\,COOH \qquad \text{(XLV)}$$



(XLVI)

The presence of four *trans*-ethylenic bonds in β-parinaric acid is further confirmed by the fact that the infrared band at 999 cm^{-1} due to such bonds is four times as intense as the 968 cm^{-1} band due to the *trans*-double bond in elaidic acid, and 40% more intense than the corresponding band in the infrared spectrum of α-elaeostearic acid (XXI). [11]

The infrared spectrum of α-parinaric acid also contains a band at 996 cm^{-1} due to a *trans*-ethylenic bond (together with a band at 952 cm^{-1}), the intensity of this band being half that of the corresponding band in the spectrum of the β-isomer, and double that of the band due to the *trans*-ethylenic bond in elaidic acid. It was therefore concluded that α-parinaric acid contains two *trans*-ethylenic bonds [11,124]. Since the α-isomer does not form an adduct with maleic anhydride, these bonds should be separated by one or two *cis*-ethylenic bonds. In such case α-parinaric acid may correspond to one of the three configurations — *cis-trans-cis-trans*, *trans-cis-trans-cis*, or *trans-cis-cis-trans* — but no data enabling a choice to be made among these configurations have yet been published†.

An investigation of the lipids from plants of the *Impatiens* genus revealed that the infrared spectrum of the seed oil was very similar to that of α-parinaric acid, but differed from the latter in the presence of an absorption band at 932 cm^{-1}. [124] An extremely unstable acid of m.p. 72–74°, termed impatienic acid and corresponding to parinaric acid in composition, was isolated by saponifying the oil in the cold and then rapidly recrystallising at low temperature. Its infrared spectrum was analogous to that of the original oil, but its ultraviolet spectrum was identical with that of α-parinaric acid (Table 7). When stored in a vacuum at 20° for a short while, impatienic acid changes into α-parinaric acid, the 932 cm^{-1} infrared band disappearing.

The problem of the configurations of parinaric and impatienic acids can probably be finally solved by means of the nuclear magnetic resonance spectra with appropriate synthetic models available.

5. SYNTHESES OF NATURALLY OCCURRING POLYENOIC ALIPHATIC ACIDS

In spite of the fact that conjugated polyenoic aliphatic acids are widely used in the paint and varnish industry, and that the first representatives of this class of compounds were discovered in Nature about a century ago, the synthesis of naturally occurring acids of this type has been accomplished only during recent years. And to this day triglycerides of vegetable origin serve as raw material for the manufacture of rapidly drying and durable varnishes.

This lag in synthetic work in this field is explained by the fact that the structures of most naturally occurring conjugated polyenoic acids have been established only comparatively recently. Furthermore, the presence in these compounds of a conjugated polyene system having various combinations of *cis*- and *trans*-ethylenic bonds makes them extremely unstable, with a marked tendency to undergo polymerisation, isomerisation, and oxidation. As a result, their synthesis necessitates the development of special procedures and methods, distinguished by their highly stereospecific character and the mildness of the conditions.

The methods first used to obtain these acids were based on the application of acetylenic syntheses and the Reformatskii reaction followed by dehydration and lengthening of the carbon chain. Thus stillingic acid (XLVII) and all its possible stereoisomers were synthesised in 1955 by Crombie [2] by means of the series of reactions shown in Scheme 9. Later Crombie and Jacklin used Schemes 10*a–c* to synthesise α-elaeostearic (XIX) and punicic (XXIII) acids and their stereoisomer — octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid (XLVIII) — which is not found in natural sources [4,89].

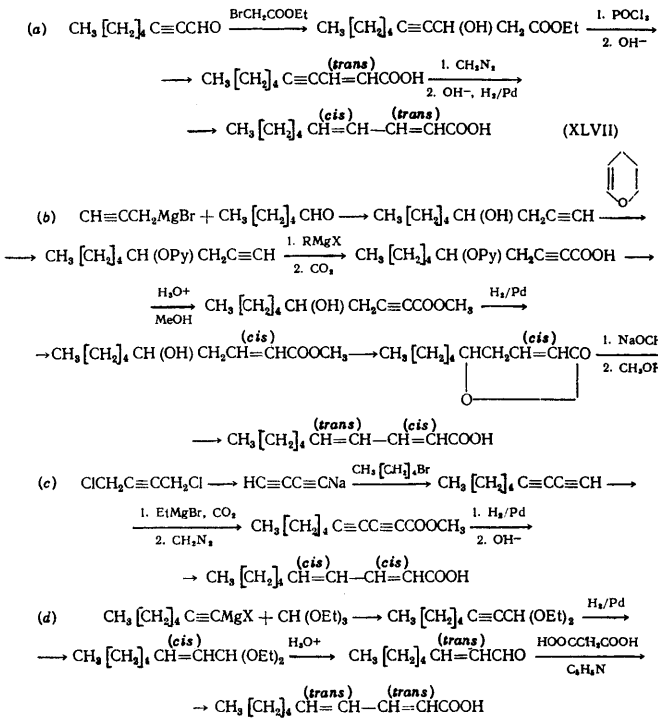
The achievement of these syntheses enabled the structures of the above naturally occurring acids to be finally established. It must be noted, however, that the above methods are characterised by many stages and low yields of the final products, while the catalytic hydrogenation of intermediate compounds containing conjugated acetylenic bonds to form *cis*-alkenes often shows little selectivity.

† *Note added in proof*. Takagi has recently obtained partial reduction products — *cis-trans*- and *trans-trans*-octadecadienoic esters — by the action of hydrazine hydrate (50° for 3 h), which causes migration of double bonds during hydrogenation, on the ethyl ester of the parinaric acid isolated from the seed oil of cultivated balsam — m.p. = 85–86° and λ_{max} = 305 nm (ε = 72400) — on the basis of which he has ascribed the *cis*-9,*trans*-11,*trans*-13,*cis*-15 configuration to parinaric acid. [136]

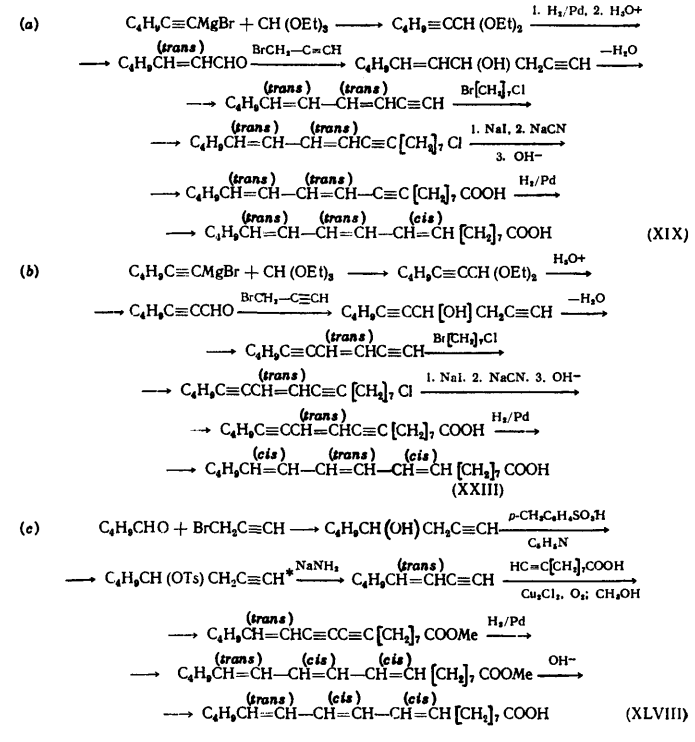
TABLE 7. Ultraviolet spectra of isomeric tetraenoic acids. [124]

Impatienic		α-Parinaric		β-Parinaric	
λ_{max}, nm	$10^{-3}\varepsilon$	λ_{max}, nm	$10^{-3}\varepsilon$	λ_{max}, nm	$10^{-3}\varepsilon$
292	45.0	292	49.5	286	59.0
305	67.7	305	72.7	299	92.8
320	58.8	320	66.3	313	87.0

Scheme 9



Scheme 10



Furthermore, these methods are of limited application, and are apparently unsuitable for the synthesis of many types of natural conjugated polyenoic aliphatic acids which have become known in recent years.

A few years ago Bergel'son et al. proposed a new method for synthesising these acids, based on the Wittig reaction, in which the general Scheme 11 was applied to the industrially available ω-chloroalkanoic acids (XLIX; R = H, X = Cl).[125-132] It was shown that the olefination of $\alpha\beta$-unsaturated aldehydes (LI) with phosphoranes (L) leads under certain conditions (in the presence of iodide ions in polar solvents) to the selective formation of a *cis*-ethylenic bond[130,131]. On the other hand, when saturated aldehydes are condensed with $\beta\gamma$-unsaturated phosphoranes (LII) in non-polar solvents, a *trans*-ethylenic bond is formed[6,132].

The application of these generalisations resulted in a new complete synthesis of α-elaeostearic acid (XIX) and of one of the isomers of calendic acid (LIII) by Scheme 12.[6,130,131] Since conjugated acids containing *cis*-ethylenic bonds are considerably more unstable than their all-*trans*-isomers, the *cis*-bond was introduced in the concluding stages. The yield of trienoic acids obtained by this method, calculated on the initial butynediol, was ~ 20%.

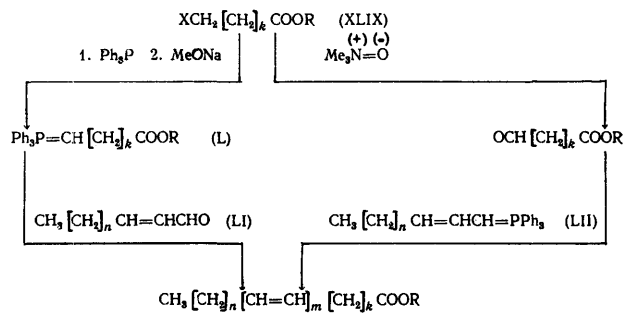
This same method was later proposed for the synthesis of octadeca-*cis*-8,*trans*-10,*trans*-12-trienoic acid (LIII) by other workers as well[133], who converted its ester, without isolating the latter, into the all-*trans*-isomer.

Two other naturally occurring conjugated trienoic acids — catalpic (XXIV) and calendic (XXVI) — were prepared for the first time by Bergel'son, Shemyakin, and their coworkers by the stereodirected *trans*-carbonyl-olefination of $\beta\gamma$-unsaturated phosphoranes according to Scheme 13.[132]

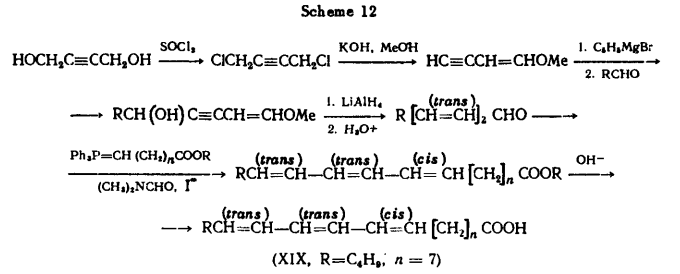
Jacarandic acid (XXXI) has been synthesised by the same investigators, using *cis*-olefination of a *cis-trans*-alkadienal in conformity with Scheme 14.[6]

* Ts = p-$CH_3C_6H_4SO_2$ (Ed. of Translation).

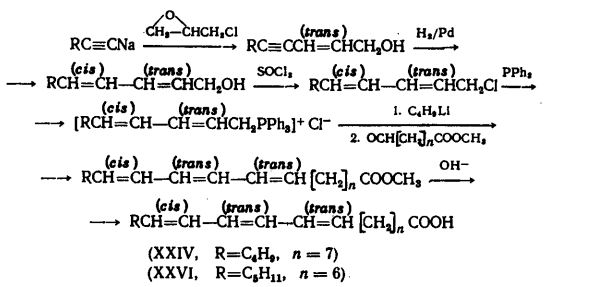
Scheme 11



Scheme 12

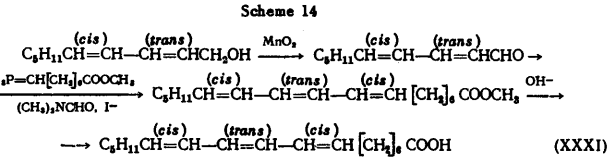


Scheme 13



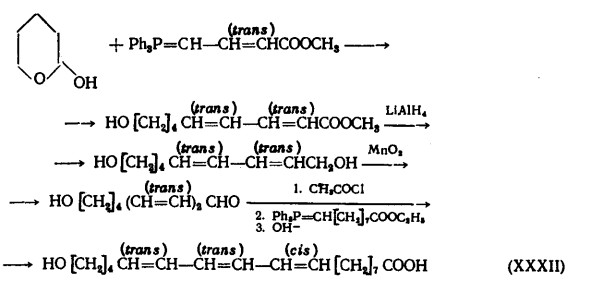
(XXIV, R=C_4H_9, $n=7$)
(XXVI, R=C_5H_{11}, $n=6$)

Scheme 14



(XXXI)

Scheme 15



(XXXII)

Bergel'son, Shemyakin, and their coworkers have synthesised the naturally occurring trienoic hydroxy-acid — kamlolenic acid (XXXII) — by successive *trans*- and *cis*--stereodirected carbonyl-olefination (Scheme 15).[134]

Dienoic and other known trienoic acids (e.g. licanic acid) can obviously be synthesised by means of stereoselective carbonyl-olefination.

1. P. L. Nicols, S. F. Herb, and W. Riemenschneider, J. Amer. Chem. Soc., 73, 247 (1951).
2. L. Crombie, J. Chem. Soc., 1007 (1955).
3. L. Crombie and J. L. Taylor, J. Chem. Soc., 2816 (1954).
4. L. Crombie and A. G. Jacklin, J. Chem. Soc., 1632 (1957).
5. M. J. Chisholm and C. Y. Hopkins, J. Org. Chem., 27, 3137 (1962).
6. V. D. Solodovnik, Candidate's Thesis, Institute of the Chemistry of Natural Compounds, Moscow, 1965.
7. M. J. Chisholm and C. Y. Hopkins, Canad. J. Chem., 38, 2500 (1960).
8. M. J. Chisholm and C. Y. Hopkins, J. Chem. Soc., 573 (1962).
9. R. S. Rassmusson, P. K. Brattain, and P. S. Zucco, J. Chem. Phys., 15, 135 (1947).
10. L. J. Bellamy, "The Infrared Spectra of Complex Molecules" (Translated into Russian under the Editorship of D. N. Shigorin), Inostr. Lit., Moscow, 1957, p. 57.
11. N. H. Ahlers, R. A. Brett, and N. G. McTaggart, J. Appl. Chem., 3, 433 (1953).
12. J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd, and D. H. Wheeler, J. Amer. Oil Chemists' Soc., 29, 229 (1952).
13. W. D. Gelmer and J. A. Solomons, J. Amer. Chem. Soc., 75, 3430 (1953).
14. D. Craig, J. Amer. Chem. Soc., 65, 1006 (1943).
15. L. Henne and A. Turk, J. Amer. Chem. Soc., 64, 827 (1942).
16. R. F. Paschke, W. Tolberg, and D. H. Wheeler, J. Amer. Oil Chemists' Soc., 30, 97 (1953).
17. W. G. Bickford, E. F. DuPré, C. H. Mack, and R. T. O'Connor, J. Amer. Oil Chemists' Soc., 30, 97 (1953).
18. H. Wexler, Chem. Rev., 64, 591 (1964).
19. N. P. Butasku, Trudy Odessk. Univ., Sbornik Khim. Fak., No. 3, 33 (1953).
20. J. E. Myers, J. P. Rass, and G. O. Burr, J. Amer. Oil. Chemists' Soc., 18, 107 (1941).
21. R. F. Paschke, J. E. Jackson, and D. H. Wheeler, Ind. Eng. Chem., 44, 1113 (1952).
22. T. F. Bradley and W. B. Johnston, Ind. Eng. Chem., 32, 802 (1940).
23. R. F. Paschke, L. E. Peterson, and D. H. Wheeler, J. Amer. Oil Chemists' Soc., 41, 723 (1964).
24. T. F. Bradley and W. B. Johnston, Ind. Eng. Chem., 33, 86 (1941).
25. H. Brunner and D. R. Tucker, J. Appl. Chem., 1, 563 (1951).
26. W. M. Potts, Paint Oil Chem. Rev., 109, No. 25, 16 (1946).
27. P. T. Huang, R. T. Holman, and W. M. Potts, J. Amer. Oil Chemists' Soc., 26, 405 (1949).
28. J. Devine, J. Sci. Food Agric., 1, 88 (1950).
29. T. P. Hilditch, J. Oil Colour Chemists' Assoc., 32, 5 (1949).
30. A. Crossley and T. P. Hilditch, J. Chem. Soc., 3353 (1949); 4613 (1952).
31. A. Crossley and T. P Hilditch, J. Sci. Food Agric., 4, 38 (1953).
32. D. P. Hanks and W. M. Potts, J. Amer. Oil Chemists' Soc., 28, 292 (1951).
33. R. T. Holman and D. P. Hanks, J. Amer. Oil Chemists' Soc., 32, 356 (1955).
34. A. L. Markman and M. D. Bodnya, Zhur. Obshch. Khim., 27, 2293 (1957).
35. B. Sreenivasan, J. B. Brown, E. P. Jones, V. L. Davison, and J. Nowakowska, J. Amer. Oil Chemists' Soc., 39, 255 (1962).
36. F. R. Earle, C. A. Glass, G. C. Geisinger, I. A. Wolff, and Q. Jones, J. Amer. Oil Chemists' Soc., 37, 440 (1960).
37. C. Y. Hopkins and M. J. Chisholm, Chem. and Ind., 2064 (1962).
38. C. Y. Hopkins and M. J. Chisholm, J. Amer. Oil Chemists' Soc., 41, 42 (1964).
39. J. D. von Mikusch, J. Amer. Chem. Soc., 64, 1580 (1942).
40. M. J. Chisholm and C. Y. Hopkins. Chem. and Ind., 1154 (1959).
41. F. R. Earle, I. A. Wolff, and Q. Jones, J. Amer. Oil Chemists' Soc., 37, 254 (1960).
42. C. R. Smith, T. L. Wilson, E. H. Melvin, and I. A. Wolff, J. Amer. Chem. Soc., 82, 1417 (1960).
43. S. Takei, I. Yamane, and T. Sekiguchi, Jap. P. 2270 (1960); Chem. Abs., 54, 25 907c (1960).
44. M. J. Diamond, R. E. Knowles, R. G. Binder, and L. A. Goldblatt, J. Amer. Oil Chemists' Soc., 41, 430 (1964).
45. F. R. Earle, K. L. Mikolajczak, and I. A. Wolff, J. Amer. Oil Chemists' Soc., 41, 345 (1964).
46. L. J. Morris, R. T. Holman, and K. Fontell, J. Amer. Oil Chemists' Soc., 37, 327 (1960).
47. S. Cloez, Compt. rend., 81, 469 (1875); 82, 501 (1876); 83, 943 (1876).
48. S. Cloez, Bull. Soc. chim. France, [2], 26, 286 (1876); [2], 28, 23 (1877).
49. L. Maquenne, Compt. rend., 135, 696 (1902).
50. R. S. McKinney and G. S. Jamieson, Oil and Soap, 14, 2 (1937).
51. R. L. Holmes, F. C. Pack, J. C. Minor, and R. S. McKinney, J. Amer. Oil Chemists' Soc., 31, 417 (1954).
52. R. T. O'Connor, D. C. Heinzelman, R. S. McKinney, and F. C. Pack, J. Amer. Oil Chemists' Soc., 24, 212 (1947).
53. T. P. Hilditch and J. P. Riley, J. Soc. Chem. Ind., 65, 74 (1946).
54. R. W. Planck, F. E. Pack, and D. B. Skau, U. S. Dept. Agric., Bur. Agric. and Ind. Chem., Circular AIC-317 (1952).

55. R.S. McKinney and G.S. Jamieson, Oil and Soap, 12, 146 (1935).
56. E.D.G. Frahm and D.R. Koolhaas, Rec. Trav. chim., 58, 277 (1939).
57. G.S. Jamieson and W.G. Rose, Oil and Soap, 20, 202 (1943).
58. A. Uzzan, J. Inform. Acides Gras Dérivés, 47 (1961).
59. A. Mandelowits, Thesis, University of Liverpool, 1952, p.150.
60. S.V. Puntambekar, Proc. Indian Acad. Sci., 35A, 57 (1952).
61. A. Steger and J. van Loon, Fette u. Seifen, 49, 769 (1942).
62. J. Riley, J. Chem. Soc., 12 (1950).
63. A. Steger and J. van Loon, Rec. Trav. chim., 53, 197 (1934).
64. N. Ivanov, Bull. Soc. chim. France, [5], 11, 404 (1944).
65. A. Steger and J. van Loon, Rec. Trav. chim., 57, 620 (1938).
66. A. Steger and J. van Loon, Rec. Trav. chim., 54, 988 (1935).
67. R.T. O'Connor, D.C. Heinzelman, R.S. McKinney, and F.C. Pack, J. Amer. Oil Chemists' Soc., 24, 212 (1947) [This is identical with Ref. 52].
68. R. Maier and R.T. Holman, Biochemistry, 3, 270 (1964).
69. J.P. Verma and J.S. Aggarwal, J. Indian Chem. Soc., 33, 357 (1956).
70. M.J. Chisholm and C.Y. Hopkins, Canad. J. Chem., 42, 560 (1964).
71. C.Y. Hopkins and M.J. Chisholm, Canad. J. Chem., 40, 2078 (1962).
72. R.S. Morrell and H. Samuels, J. Chem. Soc., 2251 (1932).
73. K.H. Bauer and E. Rohrbach, Chem. Umschau Gebiete Fette, Öle, Wachse und Harze, 35, 197 (1928).
74. J. van Loon, Rec. Trav. chim., 50, 32 (1931).
75. R.A. Allen and A.A. Kiess, J. Amer. Oil Chemists' Soc., 33, 419 (1956).
76. M.L. Woltemate and B.F. Daubert, J. Amer. Chem. Soc., 72, 1233 (1950).
77. P.W. Planck, F.C. Pack, D.C. Heinzelman, M.F. Stansbury, and R.T. O'Connor, J. Amer. Oil Chemists' Soc., 30, 598 (1953).
78. T. Takagi and B.M. Craig, J. Amer. Oil Chemists' Soc., 41, 660 (1964).
79. S. Fokin, Zhur. Russ. Fiz.-Khim. Obshch., 45, 283 (1913).
80. R. Majima, Ber., 42, 674 (1909).
81. J. Böeseken and H.J. Ravenwaay, Rec. Trav. chim., 44, 241 (1925).
82. J. Böeseken and H.J. Ravenwaay, Proc. k. ned. Akad. Wetenschap., 28, 386 (1925).
83. A. Eibner and K. Rossmann, Chem. Umschau Gebiete Fette, Öle, Wachse und Harze, 35, 197 (1928).
84. R.S. Morrell and S. Marks, J. Oil Colour Chemists' Assoc., 12, 183 (1929).
85. R.S. Morrell and W.R. Davis, J. Soc. Chem. Ind., 55, 237 261 (1936).
86. R.S. Morrell and W.R. Davis, Trans. Faraday Soc., 32, 209 (1936).
87. I.J. Rinkes, Rec. Trav. chim., 62, 557 (1943).
88. D.H. Wheeler, Official Digest Fed. Paint Varn. Prod. Clubs, No. 332, 661 (1951).
89. L. Crombie and A.G. Jacklin, Chem. and Ind., 486 (1955).
90. Y. Toyama, N.H.E. Ahlers, A.C. Dennison, and L.A. O'Neill, Nature, 173, 1045 (1954).
91. Y. Toyama, and T. Tsuchyia, J. Soc. Chem. Ind., Japan, 38, 182 B (1935).
92. N.H.E. Ahlers and N.G. McTaggart, J. Sci. Food Agric., 5, 75 (1954).
93. H.P. Kaufmann, J. Baltes, and H. Büter, Ber., 70B, 2535 (1937).
94. N.H.E. Ahlers and A.C. Dennison, Chem. and Ind., 603 (1954).
95. P. Soni and J.S. Aggarwal, J. Sci. Ind. Res., India, 8B, 150 (1949).
96. F.R. Earle, I.A. Wolff, and C.A. Glass, J. Amer. Oil Chemists' Soc., 39, 381 (1962).
97. J.S. Aggarwal, S.S. Bhatnagar, P. Narain, and Karimullah, J. Sci. Ind. Res., India, 7B, 136 (1948).
98. S.C. Gupta, S.S. Gupta, and J.S. Aggarwal, J. Sci. Ind. Res., India, 12B, 240 (1953).
99. S.C. Gupta, S.S. Gupta, and J.S. Aggarwal, J. Amer. Oil Chemists' Soc., 31, 287 (1954).
100. S.V. Puntambekar, Proc. Indian Acad. Sci., 35A, 57 (1952).
101. S. Das Gupta, V.N. Sharma, and J.S. Aggarwal, J. Sci. Ind. Res., India, 11B, 463 (1952).
102. L. Crombie and J.L. Taylor, J. Chem. Soc., 2816 (1954) [This is identical with Ref. 3].
103. S. Das Gupta and J.S. Aggarwal, J. Sci. Ind. Res., India, 13B, 449, 889 (1954).
104. S. Das Gupta and J.S. Aggarwal, J. Amer. Oil Chemists' Soc., 32, 501 (1955).
105. N.H.E. Ahlers and F.D. Gunstone, Chem. and Ind., 1219 (1954).
106. F. Wilbron, Chem.-Ztg., 55, 434 (1931).
107. J. van Loon and A. Steger, Chem. Umschau Gebiete Fette, Öle, Wachse und Harze, 37, 337 (1930).
108. W.G. Rose and G.S. Jamieson, Oil and Soap, 20, 227 (1948).
109. M. Sessler and P.A. Rowen, Chem. Weekblad, 36, 208 (1939).
110. K.S. Markley, "Fatty Acids", New York, 1960, Vol. 1.
111. A. Steger and J. van Loon, Rec. Trav. chim., 60, 13 (1941).
112. C.P.A. Kappelmeier, Fettchem. Umshau, 42, 145 (1935).
113. W.B. Brown and E.H. Farmer, J. Chem. Soc., 1632 (1935).
114. R.S. Morrell and W.R. Davis, J. Chem. Soc., 1481 (1936).
115. P.R. Jefferies and E.R. Knox, Austral. J. Chem., 14, 628 (1961).
116. J. Attenburrow, A.F.B. Cameron, J.H. Chapman, R.M. Evans, B.A. Hems, A.B.A. Jansen, and T. Walker, J. Chem. Soc., 1094 (1952).
117. M. Tsujimoto and H. Koyanagi, J. Soc. Chem. Ind., Japan, 36, 110B, 673B (1933).
118. E.H. Farmer and E. Sunderland, J. Chem. Soc., 759 (1935).
119. M. Tsujimoto, J. Soc. Chem. Ind., Japan, 39, 116B (1936).
120. H.P. Kaufmann, J. Baltes, and S. Funke, Fette u. Seifen, 45, 302 (1938).
121. T. Tutiya, J. Soc. Chem. Ind., Japan, 61, 717 (1940).
122. H.P. Kaufmann and M. Keller, Chem. Ber., 81, 152 (1948).
123. H.P. Kaufmann, Chem. Ber., 81, 159 (1948).
124. H.P. Kaufmann and R.K. Sud, Chem. Ber., 92, 2797 (1959).
125. L.D. Bergel'son, V.A. Vaver, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1900 (1960).
126. L.D. Bergel'son, V.A. Vaver, L.I. Barsukov, and M.M. Shemyakin, Dokl. Akad. Nauk SSSR, 143, 111 (1962).
127. L.D. Bergel'son, V.A. Vaver, L.I. Barsukov, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1053 (1963).
128. L.D. Bergel'son and M.M. Shemyakin, Tetrahedron, 19, 149 (1963).
129. L.D. Bergel'son and M.M. Shemyakin, Angew. Chem. (Internat. Ed.), 3, 250 (1964).
130. L.D. Bergel'son, V.D. Solodovnik, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1315 (1962).
131. L.D. Bergel'son, V.D. Solodovnik, E.V. Dyatlovitskaya, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 683 (1963).
132. L.D. Bergel'son, V.D. Solodovnik, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 843 (1967).
133. N. Petragnani and G. Schill, Chem. Ber., 97, 3293 (1964).
134. L.D. Bergel'son, E.V. Dyatlovitskaya, and M.M. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., 2003 (1964).
135. T. Takagi, J. Amer. Oil Chemists' Soc., 43, 249 (1966).

Institute of the Chemistry of Natural Compounds, USSR Academy of Sciences, Moscow