A Systematic Characterization of the Reversion Flavor of Soybean Oil [1, 2]

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Abstract

The volatile flavor compounds in a reverted soybean oil with a peroxide number of 4.3 meq/kg were isolated by a semicontinuous countercurrent vacuum steam-distillation process, fractionated by repeated gas chromatography, and identified by infrared and mass spectrometry. A total of 71 compounds were identified, which included 19 acids, 39 nonacidic compounds, and 13 tentatively identified compounds. The acids consisted of eight normal saturated acids, nine α,β-unsaturated acids, a branch-chain acid, one hydroxy acid, two keto acids, three lactones, and one aromatic acid. The nonacidic compounds consisted of two esters, eight normal saturated aldehydes, two branched-chain aldehydes, five 2-enals, three dienals, eight ketones, eight alcohols, six hydrocarbons, and four aromatic compounds.

The mechanism of formation of the identified compounds indicated that they were mostly primary or secondary autoxidation products of the hydroperoxides of the unsaturated fatty esters. Since many of the identified compounds were produced from oleic and linoleic acids, it is doubtful that linolenic acid was solely responsible for the reversion flavor.

Of the compounds identified two are of unusual interest. They are 1-decyne and 2-pentyl furan. The former is the first acetylenic compound reported as the autoxidation products of unsaturated fatty esters which contained only double bonds. The latter imparts to an oil at concentrations of 5–10 ppm a beany and grassy flavor reminiscent of that of a reverted soybean oil. Since this compound is postulated as being produced by the autoxidation of linoleic acid, it is suggested that the presence of linolenic acid catalyzes the autoxidation of linoleic acid and possibly alters the decomposition pattern of its hydroperoxides.

Introduction

THE SPECTACULAR INCREASE in the production of soybean oil has made it the most abundant fat for food use in the world. Recent statistics (1) show that the amount of soybean oil consumed in foods in the United States is approximately three times that of cottonseed oil, its nearest vegetable oil competitor, and more than 12 times that of corn oil. However soybean oil and many products containing soybean oil tend to develop an undesirable flavor and odor known as reversion when the peroxide number is still as low as a few meq/kg. This reversion flavor is characterized as beany, grassy, fishy, painty, or haylike.

During the past decade the flavor stability of soybean oil has been greatly improved because of the progress made in refining and processing technology. A properly processed soybean oil of today, particularly the hydrogenated soybean oil, is suitable for many food purposes. However soybean oil and even hydrogenated soybean oil still have the tendency to revert. The mechanism of this phenomenon has not been completely understood. Durkee (2) was one of the first to suggest linolenic acid as the precursor of the reversion compounds. Additional investigations (3,4) have supported this theory. Yet there have also been a number of reports (5,6,7) which contradicted this theory.

Another theory proposed by those who were largely interested in the edible use of linseed oil during World War II was that "insolinoleic" acid formed during the hydrogenation was the precursor of reversion flavor (8). Lips et al. (9) however found that no improvement in flavor stability occurred with decreasing concentrations of isolinoleic acid.

Mattil (10) was the first to suggest that the unsaponifiable fraction of soybean oil was responsible for the reversion flavor, but later investigations (11, 12) have shown that the unsaponifiable matter present in soybean oil does not function as a precursor of the reversion flavor.

Studies on flavor reversion of soybean oil indicated that its precursors must possess the following characteristics: a) they must be more readily formed in soybean oil than in nonreverting oils; b) they cannot be completely removed by present refining and hydrogenation practices; c) before breakdown they do not possess the flavor characteristic of reverted soybean oil; and d) their breakdown is not inhibited by antioxidants and can take place under a high vacuum or under inert gases. Such a precursor was first theorized by Chang and Kummerow (13,14). They proposed that oxidative polymers of linoleic and linolenic acid might be precursors of reversion flavor. Their later work (15) demonstrated that the oxidative polymers of soybean oil possessed the characteristics of a suitable precursor. Holm et al. (16) supported this theory, in finding that the high-molecular-weight, unsaturated carbonyl compounds, isolated from oxidized rapeseed oil, had no distinctive taste themselves yet gave rise to an intense flavor when heated. Moreover the flavor stability of an oil decreased rapidly with an increasing quantity of these substances. They were not reduced by hydrogenation and gave poor flavor stability to hardened fats. Evans et al. (17) also showed that the nonvolatile carbonyl compounds obtained from heating oxidized soybean oil, when added to a fresh soybean oil, gave a lower initial flavor score and an oil of poorer flavor stability.

In order to understand the mechanisms involved in the development of reversion flavor in soybean oil, various attempts have been made to identify the compound or compounds which are responsible for this off-flavor. Daubert and his co-workers were the first to make such attempts. They identified acetaldehyde,

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2-heptenal, and 2,4-decadienal in highly reverted soybean oils (18,19). Kawahara and Dutton identified acetaldehyde, propanal, 2-pentenal, and hexanal in a highly autoxidized soybean oil (20).

The reverted-but-not-rancid soybean oil was first studied by Von Pezold (21). He identified acetaldehyde, propanal, and 2-pentenal, also tentatively identified butanal, pentanal, 2,4-heptadienal, and/or 2,4-octadienal. Hoffmann used a slightly autoxidized soybean oil and identified saturated aldehydes from C_3 to C_6, 3-*cis*-hexenal, 3-*trans*-hexenal, and 2t, 4t and 2 t, 4c heptadienals and octadienals (22,23). He claimed that 3-*cis*-hexenal is responsible for the "green bean" flavor of the reverted soybean oil.

The genuine reversion flavor of soybean oil was first isolated by Chang, who used a semicontinuous countercurrent vacuum steam-distillation process (24). He and his co-workers identified ethyl formate, ethyl acetate, ethanol, butanal, 2-heptenal, and 2-heptanone in these isolated volatile flavor compounds (25). Later Mookherjee and Chang identified 21 monocarbonyl compounds in a reverted soybean oil with a peroxide number of only 2.7 meq/kg (26). No compound has been isolated and identified to date to which the characteristic reversion flavor may be ascribed. The present paper reports a comprehensive systematic identification of the volatile flavor compounds which have been isolated from a reverted-but-not-rancid soybean oil.

Experimental Section

Isolation of Reversion Flavor. Sixty-five gallons of a commercially refined and deodorized soybean oil were used for this investigation. The oil was packed in clear glass gallon jugs by filling them to the neck and then tightly closing them. They were aged at room temperature under diffused daylight until they developed a peroxide number of 4.3 meq/kg and a medium-strong reversion flavor but no rancid flavor. The volatile flavor compounds in this oil were isolated by the semicontinuous countercurrent vacuum steam-distillation process reported by Chang (24). The amount of isolated volatile compounds was approximately 10 ppm of the oil.

Preliminary Fractionation. The isolated reversion flavor was separated into acidic and nonacidic compounds by extracting the ethyl ether solution of the isolated volatile flavor compounds with 10% aqueous sodium carbonate solution. The acidic compounds were then converted into methyl esters by the use of diazomethane (27). The method consisted essentially of bubbling generated diazomethane gas through the ethyl ether solution of the free acids. The reaction was catalyzed with water and proceeded to completion in 15 min at 20C.

Investigation of this methylation procedure with a solution of pure crotonic, α-hydroxyisobutyric and α-ketobutyric acids showed no side reaction. Recoveries of this method were found to be 90% when pure caprylic and capric acids were methylated.

Gas Chromatography. The methyl esters of the acidic compounds were fractionated with a Beckman GC-2A Gas Chromatograph by using a 6-ft × ¼-in. OD aluminum column, packed with 20% stabilized DEGS on 70/80 mesh Anakrom ABS (Analabs, Hamden, Conn.) at a helium flow rate of 80 ml/min. The temperature was nonlinearly programmed from 50 to 200C in 14 min with a Thermotrac Temperature Programmer. The 18 fractions thus obtained were individually collected with a specially designed fraction collector (28). Each of the collected fractions was rechromatographed with an 8-ft × ¼-in. OD aluminum column, packed with 20% methyl silicone SE-30 on 70/80 mesh Anakrom ABS. The temperature was programmed nonlinearly at an optimum rate for each fraction to obtain the highest resolution. Each of the rechromatographed fractions was then collected and submitted to the identification procedure.

The nonacidic compounds were gas-chromatographed into six broad fractions with an Aerograph A-90-P2 Gas Chromatograph, using a 10-ft × ⅜-in. OD aluminum column which was packed with 20% methyl silicone SE-30 on 60/80 mesh silylated Chromosorb W (Wilkens Instrument and Research Inc., Walnut Creek, Calif.). A nonlinear programming rate of 55 to 200C in 14 min gave the best resolution. Each of the six broad fractions was collected with a specially designed fraction collector (29) and rechromatographed with a Beckman GC-2A Gas Chromatograph, using an 8-ft × ¼-in. OD aluminum column which was packed with 15% Carbowax 1000 on 70/80 mesh Anakrom ABS. The temperature was nonlinearly programmed for each fraction to obtain maximum resolution. A total of 57 rechromatographed fractions was obtained, each of which was again rechromatographed by using an 8-ft × ¼-in. OD aluminum column which was packed with 20% methyl silicone SE-30 on 70/80 mesh Anakrom ABS. The temperature was linearly programmed from 50 to 200C at 10C/min. A total of 251 fractions was thus collected and submitted to the identification procedure.

Identification of Gas Chromatographic Fractions. The gas chromatographic fractions were identified by their infrared and mass spectra. The techniques for the determination of infrared and mass spectra of gas chromatographic fractions have been reported previously (30). The chemical structure postulated for a gas chromatographic fraction by the interpretation of its infrared and mass spectra was considered as tentative. If the postulated structure was confirmed by comparing the retention time of the authentic compound with that of the gas chromatographic fraction on two different stationary phases, it was then considered as identified. Where the authentic compound of a particular carbon number was not available, homologous plots of log retention time against carbon number were prepared on two different stationary phases by using available compounds of the same homologous series. The carbon number of the fraction was then determined from the homologous plots.

Results and Discussion

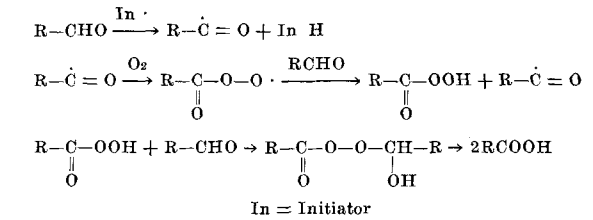
The total volatile compounds isolated from the reverted-but-not-rancid soybean oil had a strong true reversion odor and flavor. When the isolated volatile flavor compounds were added to a freshly deodorized bland corn oil, all the members of an expert organoleptic panel identified the sample as a reverted soybean oil. During the isolation process the oil was only exposed to 70C for 5½ min under vacuum. Since hydroperoxides could not be formed in a significant amount under these conditions and since the peroxide number of the oil remained as 4.3 meq/kg before and after the steam stripping, it is reasonable to assume that no further decomposition with the formation of volatile decomposition products as artifacts took place.

Both the acidic and nonacidic fractions of the isolated reversion flavor had strong odors and flavors. The odor and flavor of the nonacidic fraction were more reminiscent of those of a reverted soybean oil. Nevertheless it is possible that the acidic compounds also contribute to the total odor and flavor of a reverted soybean oil.

A total of 71 compounds were identified in the volatile compounds isolated from a reverted soybean oil. Twenty-two of these compounds were acidic (Table I), and 49 were nonacidic (Table II). The infrared and mass spectra of some of these compounds which have not been published previosly are shown in Figures 1A–1C and Figures 2A–2B respectively.

Of the 71 compounds identified, two are of unusual interest: one is 1-decyne, and the other is 2-pentyl furan. The identification of these two compounds and the proposed machanisms of their formation have been reported previously (31,32). The 1-decyne is of unusual interest because it is the first acetylenic compound reported as an autoxidative decomposition product of fatty esters which have only double bonds. The 2-pentyl furan is of unusual interest because of its odor and flavor characteristics. This compound itself in concentrated form has a licorice odor but not beany and grassy odors. Its flavor threshold in oil at room temperature is approximately 1 ppm. At concentrations of 1–10 ppm this compound imparts to an oil a characteristic beany and grassy odor and flavor reminiscent of those of a reverted soybean oil. Expert organoleptic panels at four different laboratories consistently identified a bland freshly deodorized cottonseed oil containing 5 ppm of 2-pentyl furan as a reverted soybean oil. It was therefore concluded that 2-pentyl furan is predominantly responsible for the reversion flavor of soybean oil, particularly that which developed when the oil has been exposed to light.

The mechanisms of the formation of acidic compounds in fats and oils have been thoroughly discussed in a previous paper (33). However, under the conditions in which reversion flavor was developed, the acids were most probably formed through the secondary autoxidation of corresponding aldehydes by a peracid mechanism (34,35):



In = Initiator

The mechanisms of the formation of hydrocarbons, aldehydes, ketones, lactones, and aromatic compounds, through the decomposition of the hydroperoxides of unsaturated fatty esters, have been reviewed and postulated by Chang and his co-workers (26,30,33, 36,37). Furthermore the mechanisms of the formation of 1-decyne and 2-pentyl furan from the autoxidative decomposition of oleic and linoleic acids respectively have been published previously (31,32).

1-Octen-3-ol was first identified in fats and oils by Hoffmann (38), who postulated that it was formed from linoleic acid through the formation of a hemiacetal. A new mechanism is proposed in which this compound may be formed through the following sim-

TABLE I

Volatile Acidic Compounds Identified in Reverted Soybean Oil

	Peak No.[1]	Identified as	Peak size[2]
I.	Normal saturated acids		
	1-	Acetic acid	S
	2-B	Propanoic acid	M
	3-D	Butanoic acid	L
	4-D	Pentanoic acid	L
	5-J	Hexanoic acid	L
	6-G	Heptanoic acid	L
	8-F	Octanoic acid	L
	10-E	Nonanoic acid	S
II.	Normal unsaturated acids		
	4-B	2, *cis*-Butenoic acid	S
	5-D	2, *cis*-Pentenoic acid	S
	4-E	2, *cis*-Hexenoic acid	S
	8-D	2, *cis*-Octenoic acid	S
	5-B	2, *trans*-Butenoic acid	S
	5-H	2, *trans*-Pentenoic acid	S
	7-C	2, *tlans*-Hexenoic acid	S
	9-G	2, *trans*-Heptenoic acid	M
	11-F	2, *trans*-Octenoic acid	M
III.	Branch-chain acid		
	2-C	2, Methyl-propanoic acid	S
IV.	Hydroxy acid		
	15-G	3-Hydroxy-heptanoic acid[3]	S
V.	Keto acids		
	15-E	4-Keto-hexanoic acid[3]	S
	15-H	7-Keto-octanoic acid[3]	S
VI.	Aromatic acid		
	13-F	Benzoic acid	S

[1] Numerals and letters indicate the number of peak during original chromatography and rechromatography respectively.
[2] XL—extra large, peak height over 1,000 recorder chart units.
L—large, peak height 760–1,000 recorder chart units.
M—medium, peak height 330–760 recorder chart units.
S—small, peak height 0–330 recorder chart units.
[3] Tentatively identified.

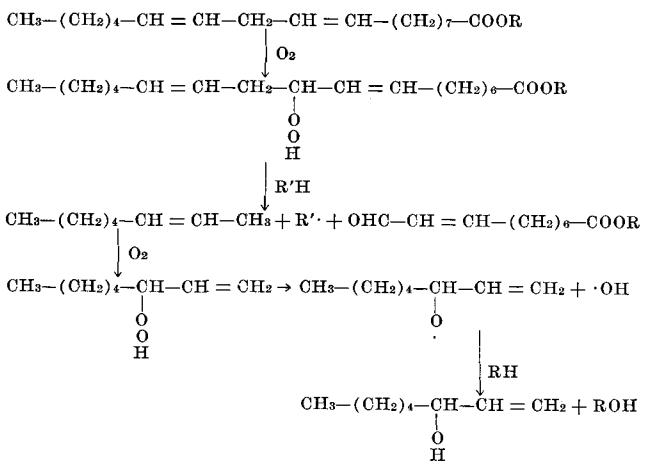
TABLE II

Volatile Nonacidic Compounds Identified in Reverted Soybean Oil

	Peak No.[1]	Identified as	Peak size[2]
I.	Aldehydes		
	1-	Acetaldehyde	S
	3-B-1	Butanal	S
	4-E-2	Pentanal	XL
	4-H-5	Hexanal	XL
	5-D-4	Heptanal	S
	5-F-8	Octanal	XL
	5-H-8	Nonanal	XL
	6-L-3	Decanal	S
	4-H-4	2-Pentanal	L
	4-J-3	2-Hexanal	S
	5-G-5	2-Heptanal	XL
	5-I-6	2-Octenal	XL
	5-K-8	2-Nonenal	XL
	5-J-2	2, *trans*-4, *cis*-Heptadienal[3]	M
	5-K-3	2, *trans*-4, *trans*-Heptadienal	XL
	5-L-5	2, *trans*-6, *trans*-Nonadienal[3]	M
	5-M-1	2, 3-Dimethyl-4-methoxy butanal[3]	S
	5-I-5	Branch-Chain 2-nonenal	S
II.	Ketones		
	5-D-3	2-Heptanone	XL
	5-F-7	2-Octanone	XL
	5-G-10	2-Nonanone	S
	5-E-6	3-Octanone[3]	S
	5-F-6	4-Octene-3-one[3]	S
	5-H-7	2-Methyl-5-Octen-4-one[3]	S
	5-H-7	3, 6-Nonadien-5-one[3]	S
	5-K-7	7-Methyl-2-Octen-4-one[3]	S
III.	Alcohols		
	1-C-0	Ethanol	XL
	2-E-0	Propanol	S
	3-H-2	Butanol	S
	4-K-2	Pentanol	XL
	5-G-2	Hexanol	S
	3-G-2	2-Pentanol	S
	3-H-3	1-Penten-3-ol	XL
	5-L-3	1-Octen-3-ol	XL
IV.	Esters		
	4-B-0	Ethyl formate	S
	2-C-2	Ethyl acetate	XL
V.	Hydrocarbons		
	5-A-3	Nonane	S
	5-B-7	Decane	S
	5-B-8	Undecane	S
	6-H-2	Dodecane	S
	5-B-6	1-Decene	S
	5-D-8	1-Decyne	XL
VI.	Lactone		
	15-C	4-Hydroxy-pentanoic acid, lactone	S
	16-C	4-Hydroxy-hexanoic acid, lactone	S
	5-P-1	4-Hydroxy-2 hexenoic acid, lactone[3]	S
VII.	Aromatic compounds		
	3-C-2	Benzene	S
	5-L-1	Benzaldehyde	S
	5-D-7	2-Pentyl furan	L
	5-E-6	Acetophenone	S

[1] The first numerals, the letters, and the second numerals indicate the number of gas chromatographic peaks during original chromatography, and first and second rechromatography respectively.
[2] XL—extra large, peak height over 1,000 recorder chart units.
L—large, peak height 760–1,000 recorder chart units.
M—medium, peak height 330–760 recorder chart units.
S—small, peak height 0–330 recorder chart units.
[3] Tentatively identified.

ple secondary autoxidation without the necessity of forming the hemi-acetal intermediate.



Examination of the mechanism of formation of the nonacidic compounds which were identified in the reversion flavor indicated that more of these compounds are originated from oleic and linoleic acids than from linolenic acids (Table III). The compound

TABLE III

Precursors of the Major Nonacidic Compounds Identified in Reversion Flavor

Linolenic acid	Linoleic acid	Oleic acid
2-Pentenal	Pentanal	Octanal
2, 4-Heptadienal	Hexanal	Nonanal
Ethanol	2-Heptenal	2-Nonenal
1-Penten-3-ol	2-Octenal	1-Decyne
Ethyl acetate	2-Heptanone	
	2-Octanone	
	Pentanol	
	1-Octen-3-ol	
	2-Pentyl furan	

which is predominantly responsible for the reversion flavor of soybean oil, 2-pentyl furan, is also postulated as originating from linoleic acid. It is possible that the reversion flavor is not entirely the result of the autoxidative decomposition of linolenic acid. However linolenic acid is more reactive than linoleic and

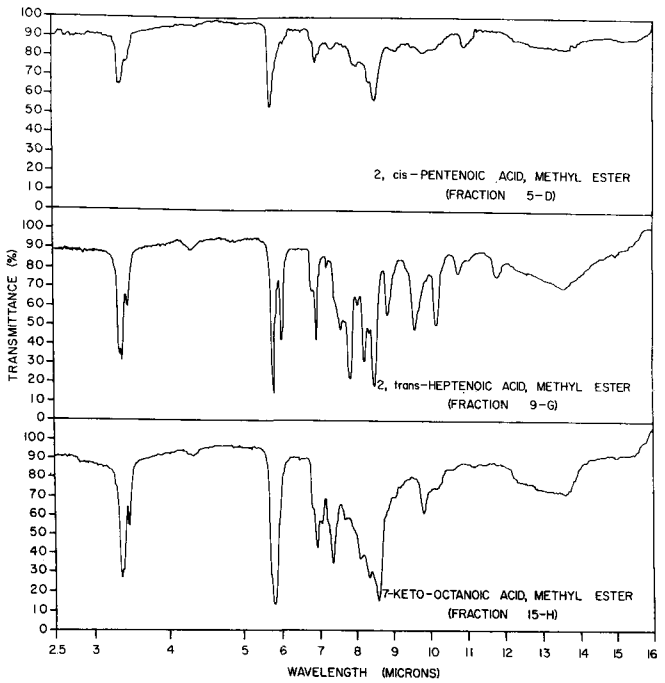


FIG. 1A. Infrared spectra of gas chromatographic fractions identified as compounds given.

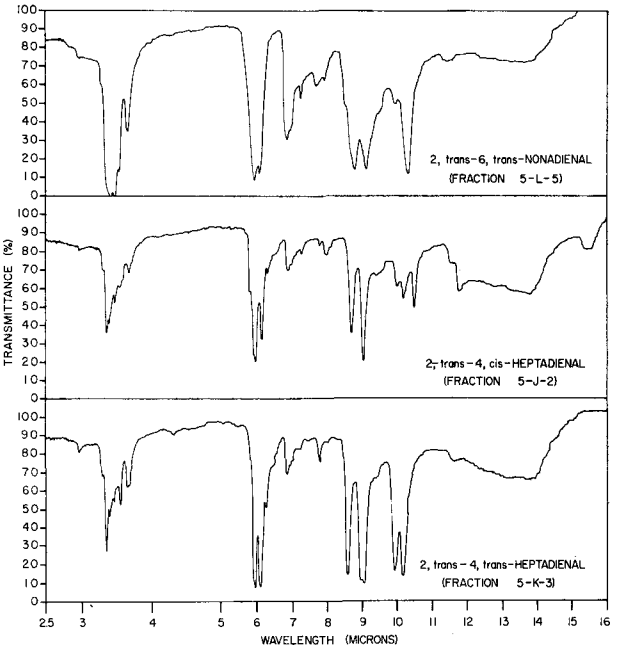


FIG. 1B. Infrared spectra of gas chromatographic fractions identified as compounds given.

oleic acids and may therefore serve as a catalyst to initiate their autoxidation.

Since 2-pentyl furan is postulated as originating from linoleic acid, it is natural to ask why this compound is formed in an amount sufficient to cause reversion flavor in soybean oil but not in cottonseed oil, which contains an approximately equal amount of linoleic acid. Further research is being conducted in this laboratory to answer the question. It is possible that the linolenic acid in soybean oil not only catalyzes the autoxidation of linoleic acid but may also alter the decomposition pattern of its hydroperoxides.

Interpretation of Infrared and Mass Spectra

2-Enoic Acids, Methyl Esters. The methyl esters

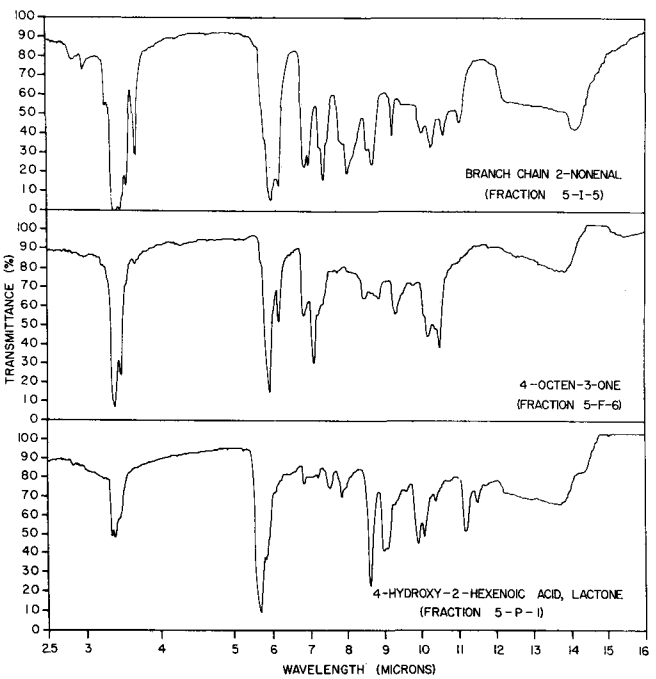


FIG. 1C. Infrared spectra of gas chromatographic fractions identified as compounds given.

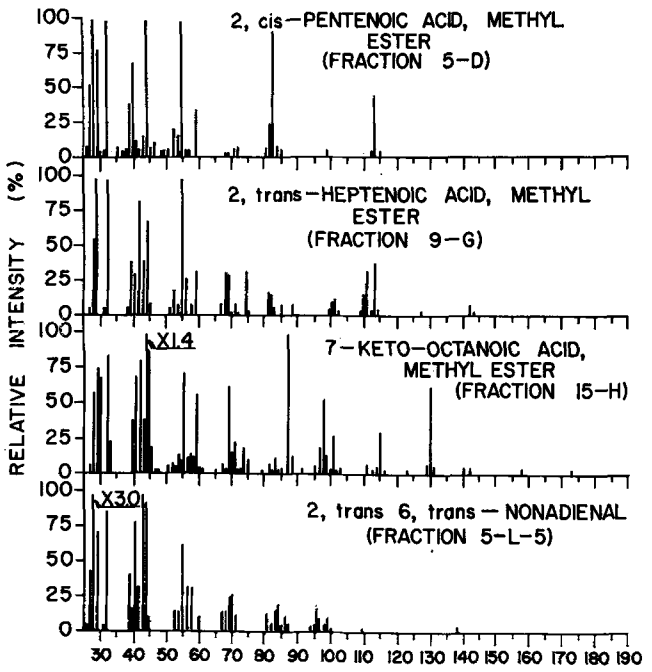


FIG. 2A. Mass spectra of gas chromatographic fractions identified as compounds given.

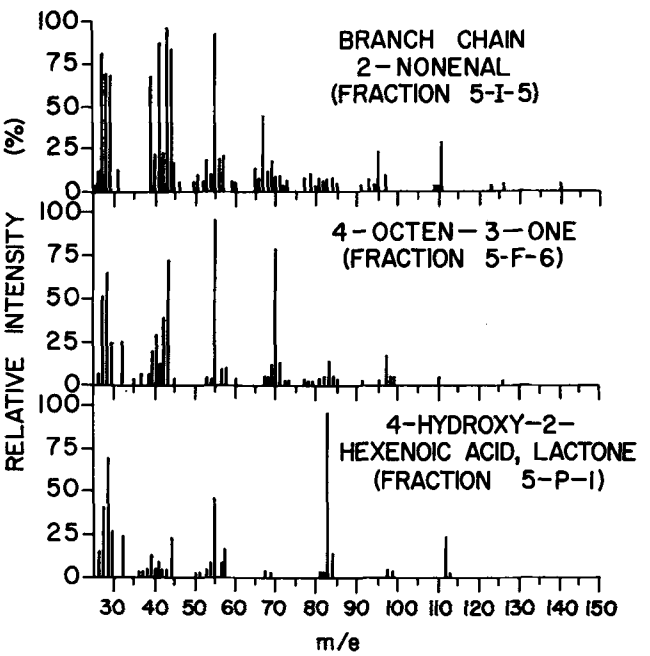


FIG. 2B. Mass spectra of gas chromatographic fractions identified as compounds given.

of 2,*trans*-enoic acids have similar infrared spectra. The same is true for the methyl esters of 2,*cis*-enoic acid although significant differences exist between the infrared spectra of these two homologous compounds. The infrared spectra of methyl 2, *cis*-pentenoate and 2, *trans*-heptenoate are shown in Figure 1A as examples. The identification of these two compounds essentially depends upon their mass spectra (Figure 2A). The mass spectrum of methyl 2, *cis*-pentenoate shows a molecular ion of m/e 114. The small peak at m/e 99 results from the fragmentation at the terminal methyl group; the charge remains on the larger fragment. The *alpha*-cleavage can readily occur adjacent to the carbonyl group of the ester yielding four ions. Of these, the butene ion (m/e 55) is of the highest intensity; much less charge remains on the m/e 59 fragment ($\oplus$ CO—O—CH_3). This indicates that the fraction is an unsaturated alkyl ester. Fragmentation on the other side of the carbonyl group gives rise to the large peak at m/e 83 or the acylium ion ($R-C\equiv\overset{\oplus}{O}$), which usually occurs in methyl esters. The remaining ion derived from this fragmentation is m/e 31 ($\oplus$O—CH_3), which abstracts a proton that gives the methyl alcohol peak at m/e 32. The β-cleavage with a γ-hydrogen transfer, which commonly occurs in saturated alkyl methyl esters, is virtually absent. However one would expect this since a double bond conjugated with the carbonyl group would prevent a cleavage of this type. The mass spectrum of methyl 2, *trans*-heptenoate shows molecular ion of m/e 142. The *alpha*-cleavage at the methoxy side of the carbonyl group gives m/e 31, which again abstracts a proton that gives methyl alcohol (m/e 32). The other fragment of this cleavage is the acylium ion which occurs at m/e 111. With α-cleavage on the alkyl side of the carbonyl group, fragment m/e 59 appears more intensely than it does in methyl 2, *cis*-pentenoate. The low intensity of fragment m/e 83 is attributable to the migration of the double bond within the alkyl chain. This migration is also evidenced by m/e 41 and m/e 55. The *beta*-cleavage could also occur after migration of the double bond, which would give rise to m/e 74 and m/e 68.

7-Keto-Octanoic Acid, Methyl Ester. The infrared spectrum (Figure 1A) showed no carbonyl group absorption other than that of an ester at 5.8 μ. Its mass spectrum (Figure 2A) showed a molecular ion of m/e 172. The large peak at m/e 130 would be attributable to the loss of ketone (P minus 42) which was formed by a rearrangement of the 7-keto group. Cleavage *gamma* to the ester carbonyl (P minus 85) would give the large peak at m/e 87. Butene ion (m/e 55) would form from the four carbon atoms between the carbonyl groups. The remaining ions present in relatively large amounts are m/e 115, resulting from cleavage β to the ketone carbonyl (P minus CH_3COCH_2), m/e 98 resulting from the rearrangement of the cleavage β to the ester carbonyl, m/e 59 resulting from the cleavage α to the ester carbonyl, and m/e 43 and m/e 129 resulting from the loss of the terminal methyl acylium ion from cleavage α to the ketone carbonyl.

2, trans-6, trans-Nonadienal. The infrared spectrum (Figure 1B) was similar to that of a 2-enal. The shifting of the carbonyl absorption (5.8 μ) and olefin absorption (6.2 μ) to a closer position of 5.95 and 6.1 μ indicated the presence of a double bond in conjugation with the carbonyl group. The infrared spectrum also resembles that of a 2, *trans*-4, *cis*-dienal because of the absorption between 8.5 and 10.5 μ. However retention times of the gas chromatograph indicated that this fraction is neither of these two classes of compounds. The mass spectrum (Figure 2A) showed a molecular ion of m/e 138, which indicated a dienal. The butene ion of m/e 55 showed the presence of a double bond in the last four carbon atoms of the nine carbon atoms chain. The ions at m/e 69 ($CH_2-CH=CH-CHO$) and m/e 70 ($CH_2=CH-CH=\underset{\underset{H}{|}}{\underset{O}{|}}{C}-H$) confirms the conclusion from the infrared spectrum that a double bond was in conjugation with the carbonyl group. Both the loss of m/e 29 and m/e 31 fragment ions in the mass

spectrum and the absorption at 3.7 μ in the infrared spectrum indicated that this fraction was an aldehyde. This fraction was tentatively identified as 2, *trans*-6, *trans*-nonadienal by the interpretation of its infrared and mass spectra.

2, trans-4, trans-Heptadienal. The infrared spectrum (Figure 1B) shows the presence of an aldehydic proton (3.7 μ) and a conjugated carbonyl group (5.95 and 6.1 μ). The carbon-to-carbon stretching pattern between 8.5 and 10.5 μ is characteristic of a 2,4-dienal. Doublets at 9.0 and 10.0 μ indicated that the two double bonds are in the *trans* configuration. Since this spectrum and the retention time of this fraction match those of the authentic compound, it is concluded that it is 2, *trans*-4, *trans*-heptadienal.

2, trans-4, cis-Heptadienal. The infrared spectrum (Figure 1B) is similar to those of 2, *trans*-4, *trans*- and 2, *trans*-6, *trans*-dienals. However closer examination shows a triplet at approximately 9.85, 10.1, and 10.4 μ, which is characteristic of a 2, *trans*-4, *cis*-dienal. Since this compound was not available, its retention time could not be compared with that of the authentic compound. Yet its retention time with methyl silicone as the stationary phase is slightly less than 2, *trans*-4-*trans*-heptadienal. This is to be expected because of the higher boiling point of the 2, *trans*-4, *trans* isomer than the 2, *trans*-4, *cis*-isomer because of geometric configurations. Furthermore the infrared spectrum has all the absorption peaks listed in a previous publication for this compound (23).

Branch-Chain 2-Nonenal. The infrared spectrum of this fraction (Figure 1C) indicated that this fraction was a branch-chain, unsaturated aldehyde by the absorptions at 7.1 and 7.4 μ (branching), 2.8 μ (enolization), 3.3, 6.2, and 10.3 μ (unsaturation), and 3.7 and 5.95 μ (aldehydic carbonyl). The combination of 6.2, 3.7, and 5.95 μ indicated that the double bond is conjugated with the aldehydic carbonyl group. The mass spectrum indicated that this fraction is a branch-chain 2-nonenal by the following ions: m/e 140 (parent ion), m/e 126 (P minus methyl), m/e 123 (P minus OH), m/e 111 (P minus CHO), m/e 43 (Propyl), m/e 39 (), and m/e 29 (ethyl or CHO).

4-Octen-3-one. The infrared spectrum (Figure 1C) suggested a conjugated *trans* unsaturated ketone from the following absorptions: 5.95 μ (carbonyl), 6.1 μ (c = c), and 10.4 μ (*trans* c = c). The closeness of 5.95 and 6.1 μ indicated that the double bond is conjugated with the carbonyl group. Its mass spectrum (Figure 2B) gave the necessary information to conclude its structure. The parent ion appeared at m/e 126. Other fragments were m/e 97 (P minus ethyl), m/e 29 (ethyl), m/e 83 (P minus propyl), m/e 43 (propyl), m/e 70 (P minus $CH_3-CH=C=O$), and m/e 55 ($CH_3-CH_2-CH=CH_2$ by rearrangement).

4-Hydroxy-2-Hexenoic Acid, Lactone. The infrared spectrum (Figure 1C) showed that this fraction was an α,β-unsaturated lactone by the absorptions at 3.4 μ (unusual C—H stretching), 5.75 μ (conjugated lactone carbonyl), and 5.95 μ (unsymetrical olefin). The mass spectrum (Figure 2B) showed ions at m/e 112 (parent ion), m/e 83 (P minus ethyl), and m/e 55 ($CH_3-CH_2-CH=CH_2$). It also contained minor peaks characteristic of the mass spectrum of α,β-unsaturated lactones (39).

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