Calculations of heats of fusion have been made, based upon all the available freezing-point data in the literature for binary systems between pairs of C_{18} fatty acids of different degrees of unsaturation, and certain trends have been dsicussed.

Acknowledgment

The authors are indebted to Dorothy C. Heinzelman for the spectrophotometric determinations of the purity of the acids.

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Flavor Reversion in Soybean Oil. VII. The Autoxidation of Isolinoleic Acid[1,2]

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THE problem of flavor reversion in fats and oils has been investigated over a period of years by many workers (1, 2), and a number of theories have been proposed to account for the development of these objectionable flavors and odors. These are generally based upon either the linolenic and polyunsaturated acid content, the non-glyceride fraction, or various nitrogenous constituents.

Previous investigators (3-7) have isolated from the deodorization condensate of reverted oils a number of saturated and unsaturated carbonyl compounds which contribute to the reversion flavors in hydrogenated and unhydrogenated materials. Recent organoleptic studies (8) have supported polyunsaturated acids as precursors of reversion products and, as suggested by Lemon (9-12) in an investigation of the hydrogenation of both linseed and perilla oils, isolinoleic acid, formed during the course of the hydrogenation, may be responsible for the presence of reversion flavors. Isolinoleic acid, by definition (13), may be a mixture of isomeric octadecadienoic acids which does not give a conjugated double bond system on isomerization with alkaline ethylene glycol as determined by the spectrophotometric procedure (14). The purpose of this work was to prepare isolinoleic acid by the partial catalytic hydrogenation of methyl linolenate and to investigate the products from the autoxidation of this compound in order to gain some insight into the reversion process and to determine, if possible, the validity of the proposal that isolinoleic acid may be a precursor of reversion products.

Experimental

Preparation of Methyl Isolinoleate. Methyl isolinoleate was prepared by the partial catalytic hydrogenation of a highly purified methyl linolenate (I.V. 260.0 ± 0.5) obtained from linseed oil linolenic acid which had been purified by bromination-debromination procedures according to the method of Frankel and Brown (15). The hydrogenation was conducted, using a Parr Medium Pressure Series 4,500 Hydrogenation Unit with limited stirring, 2.0% Harshaw Nickel Chip Catalyst Ni-0501f (0.5% nickel), a temperature of 175° ± 5°C. and a pressure of 45 ± 5 pounds. The hydrogenation was discontinued when spectroscopic examination of the reaction mixture showed negligible methyl linolenate present.

The crude methyl isolinoleate was concentrated by low temperature fractional crystallization from methanol according to the method of Rebello and Daubert (13). After removal of the solvent from the —75°C. filtrate, the residual ester was molecularly distilled to give a fraction (2 g., I.V. 170.4 ± 1.0, b.p. 55° — 7°C./3 — 4 microns pressure) which was designated as S.N. 1-2H-99. The composition of this material (theoretical I.V. 172.4), as summarized in Table I, was obtained through determination of the Iodine Value for total unsaturation, linoleic and linolenic acids by spectrophotometric procedures (14) and using methods of calculation (13) for the isolinoleic acid and combined oleic and isooleic acids.

TABLE I

Analysis of Methyl Isolinoleate (S.N. 1-2H-99)

Constituent	Percentage Composition
Methyl isolinoleate	94.8 ± 1.5
Methyl linolenate	0.5 ± 0.1
Methyl linoleate	1.5 ± 0.1
Methyl oleate and isoleate	3.2 ± 1.7

Reversion and Deodorization. The reversion and deodorization of the methyl isolinoleate was carried out, using the small scale, all-glass laboratory deodorizer previously described (4), by first heating over a 30-minute period to 200°C. under normal atmospheric conditions and then removing the reversion

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[1] Contribution No. 905 from the Department of Chemistry, University of Pittsburgh.

[2] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[3] Present address: Lucidol Division, Novadel-Agene Corporation, Buffalo, N. Y.

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products by steam distillation for one hour at 110°C. and 2-3 mm. pressure, leaving a bland oil. The mixture of water and yellow-green oily distillate was washed out of the dry ice traps at the end of each day's deodorization with aldehyde-free ethyl ether and stored at 6°C. Outside of a slight darkening of the oil there was no apparent deterioration or decrease in its ability to revert. After each five reversions and deodorizations the Peroxide Value was determined by the method of Wheeler (16) and found to vary from 0.3 to 6.7 in an irregular manner.

From 25 reversions and deodorizations carried out on 630 g. of methyl isolinoleate (S.N. 1-2H-99), there were obtained 16.1 g. of ether-soluble yellow-green liquid with an odor similar to that of reverted soybean oil and 0.3 g. of a water-soluble semi-solid pale yellow material. The ether-soluble fraction (S.N. 1-2H-103), after separation into volatile and nonvolatile products by vacuum distillation at room temperature, was further fractionated with 5% potassium carbonate solution into acid and neutral fractions. From the ether-soluble volatile fraction (0.45 g.) there were obtained 0.31 g. of neutral components and 0.05 g. of acidic material while the ether-soluble residue fraction (15.47 g.) gave 13.73 g. of neutral products and 0.87 g. of acidic material. A summary of these operations may be found in Figure 1.

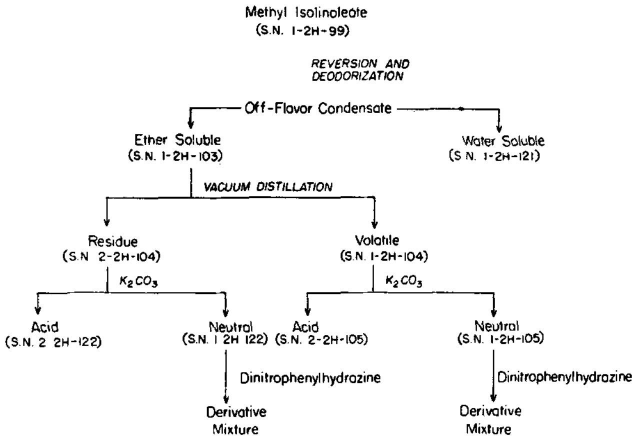

FIG. 1. Fractionation of the autoxidation products.

Organoleptic examination (17) supplemented by positive Schiff's, Tollen's, and the m-phenylenediamine test for α,β-unsaturated carbonyls (18) indicated that the reversion-like flavor components were concentrated in the ether-soluble neutral volatile and residue fractions.

Dinitrophenylhydrazone Derivatives of the Ether-Soluble Volatile Neutral Fraction

The 2,4-dinitrophenylhydrazone derivatives of this fraction (S.N. 1-2H-105) were prepared in a manner similar to that previously described (19) and then were isolated and purified by chromatography using heptane as the solvent, 0.5% ethyl ether in heptane as the developing agent and a silicic acid-Supercell (2:1) mixture as the adsorbent. The combined techniques of elution and cutting of the column were used to separate the derivatives which after chromatographing to a constant melting point were recrystallized from ethanol. From this fraction there were isolated three distinct compounds.

1. *Compound S.N. 1-2H-108.* There were obtained 35.2 mg. of a red-orange crystalline product, m.p. 142.0°-142.6°C., which analyzed C, 52.14; H, 4.70; N, 19.92. A calculation of the empirical formula gave $C_{12}H_{14}O_4N_4$ for the derivative and $C_6H_{10}O$ for the carbonyl portion. A mixed melting point with 2-hexenal-2,4-dinitrophenylhydrazone (145.0°-145.4°C.) was 145.0°-145.6°C.

The ultraviolet and infrared absorption spectra of Compound S.N. 1-2H-108 and 2-hexenal-2,4-dinitrophenylhydrazone were determined and found to be in good agreement as shown in Figures 2 and 6 respectively. The infrared absorption spectra[5] were made in a Nujol mull using a Baird Double Beam Spectrophotometer.

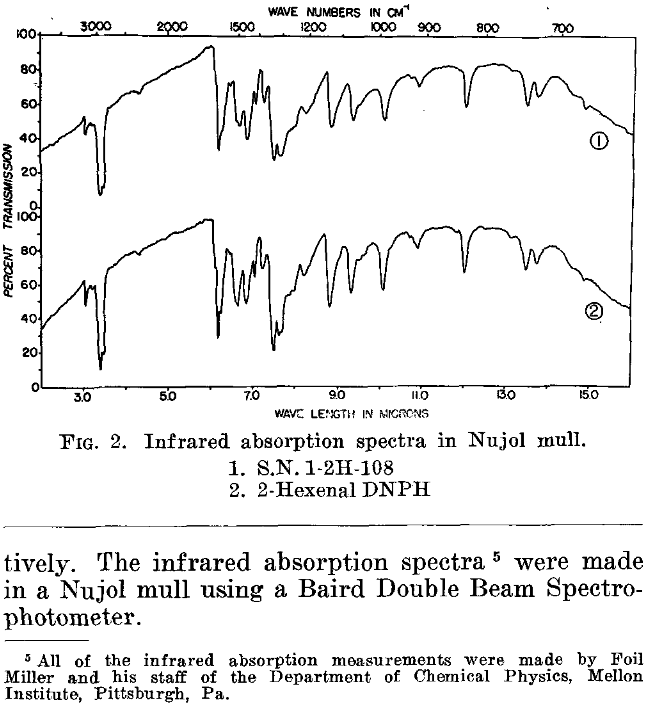

FIG. 2. Infrared absorption spectra in Nujol mull.
1. S.N. 1-2H-108
2. 2-Hexenal DNPH

TABLE II

Comparison of the Dinitrophenylhydrazone Derivatives of the Ether-Soluble Neutral Volatile Fraction

Compound	M.P. (°C.)	Mixed M.P. (°C.)	Color	Wavelength of Max. Absorption (mμ)	Formula of Hydrazone	Elemental Analyses[a] (Percentage) C	H	N	Data
S.N. 1-2H-108	142.0-142.6	145.0-145.6	red orange	377-8	$C_{12}H_{14}N_4O_4$	52.14	4.70	19.92	Found
					$C_{12}H_{14}N_4O_4$	51.79	5.03	20.13	Calcd.
2-Hexenal DNPH	145.0-145.4		red orange	377-8	$C_{12}H_{14}N_4O_4$	52.34	4.60	20.16	Found
S.N. 1-2H-135	154.3-155.0	154.0-154.5	orange	357-58	$C_9H_{10}N_4O_4$	45.38	4.26	23.15	Found
Propanal DNPH	154.2-154.7		orange	357-58	$C_9H_{10}N_4O_4$	45.40	4.20	23.51	Calcd.
S.N. 2-2H-135	125.0-125.5	125.1-125.8	yellow	361-2	$C_9H_{10}N_4O_4$	45.63	3.94	23.42	Found
Acetone DNPH	125.2-125.6		yellow	361-2	$C_9H_{10}N_4O_4$	45.40	4.20	23.51	Calcd.

[a] Microanalyses were performed by G. Stragand, Microchemical Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania.

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[5] All of the infrared absorption measurements were made by Foil Miller and his staff of the Department of Chemical Physics, Mellon Institute, Pittsburgh, Pa.

The 2-hexenal was synthesized by condensing butyraldehyde with methyl hydrogen malonate to yield methyl 2-hexenoate according to the method of Galat (20). Reduction of the ester to the alcohol with lithium aluminum hydride (21) and oxidation with dichromate to the aldehyde (22) gave 2-hexenal. The semicarbazone (m.p. 176.4°-177.2°C.), the p-nitrophenylhydrazone (m.p. 137.3°-138.0°C.), and the 2,4-dinitrophenylhydrazone (m.p. 145.0°-145.4°C.) derivatives were prepared. Delaby and Guillot-Allegre (22) found 175°-176°C. for the semicarbazone and 139°C. for the p-nitrophenylhydrazone.

2. Compound S.N. 2-2H-135. After rechromatographing a number of times, there were obtained 5.2 mg. of a yellow-orange crystalline material, m.p. 154.3°-155.0°C., which analyzed C, 45.38; H, 4.26; N, 23.15. A calculation of the empirical formula gave $C_9H_{10}O_4N_4$ for the derivative and C_3H_6O for the carbonyl compound. A mixed melting point with the 2,4-dinitrophenylhydrazone of propionaldehyde (154.2°-154.7°C.) was 154.0°-154.5°C. The ultraviolet absorption spectrum in ethanol was similar to that of the 2,4-dinitrophenylhydrazone of propionaldehyde exhibiting maximum absorption at 357-58 mμ.

3. Compound S.N. 1-2H-135. There were also isolated chromatographically 4.5 mg. of golden yellow crystalline needles, m.p. 125.0°-125.5°C. Analysis: C, 45.63; H, 3.94; N, 23.42, which gave an empirical formula of $C_9H_{10}O_4N_4$ for the derivative and C_3H_6O for the original carbonyl. A mixed melting point with acetone 2,4-dinitrophenylhydrazone (125.2°-125.6°C.) was 125.1°-125.8°C. The ultraviolet absorption spectrum in ethanol agreed well with that of the authentic 2,4-dinitrophenylhydrazone of acetone exhibiting a maximum at 361-2 mμ.

A comparison of the carbon, hydrogen, and nitrogen analyses together with some of the physical properties of the hydrazones isolated from the ether-soluble volatile neutral fraction with the 2,4-dinitrophenylhydrazones of authentic carbonyl compounds may be found in Table II.

Dinitrophenylhydrazone Derivatives of the Ether-Soluble Residue

Neutral Fraction. From the mixture of 2,4-dinitrophenylhydrazones obtained from this fraction there have been isolated and purified by chromatographic procedures six distinct compounds. Numbering these compounds in the order in which they appeared on the chromatographic column, they were designated respectively S.N. 1-2H-128, S.N. 2-2H-128, S.N. 3-2H-128, S.N. 2-2H-136, S.N. 1-2H-136, and S.N. 1-2H-134. Of these S.N. 2-2H-128, S.N. 1-2H-136, and S.N. 1-2H-134 were similar to those compounds isolated previously from the ether-soluble volatile neutral fraction and identified as the 2,4-dinitrophenylhydrazones of 2-hexenal, propionaldehyde, and acetone respectively.

1. Compound S.N. 1-2H-128. After recrystallization of this product from ethanol there were obtained 31 mg. of a red crystalline 2,4-dinitrophenylhydrazone with a m.p. of 91.5°-92.6°C. This material was rechromatographed five times after which the melting point remained constant; yield 7 mg., m.p. 94.3°-95.0°C.

An elemental analysis showed: C, 57.43; H, 5.85; N, 17.08. A calculation of the empirical formula gave $C_{16}H_{20}O_4N_4$ for the derivative and $C_{10}H_{16}O$ for the carbonyl portion.

The ultraviolet and infrared absorption spectra were determined and are shown in Figures 3 and 4 respectively. The ultraviolet absorption spectrum in ethanol shows a maximum at 377 mμ, which is characteristic of α,β-unsaturation (23).

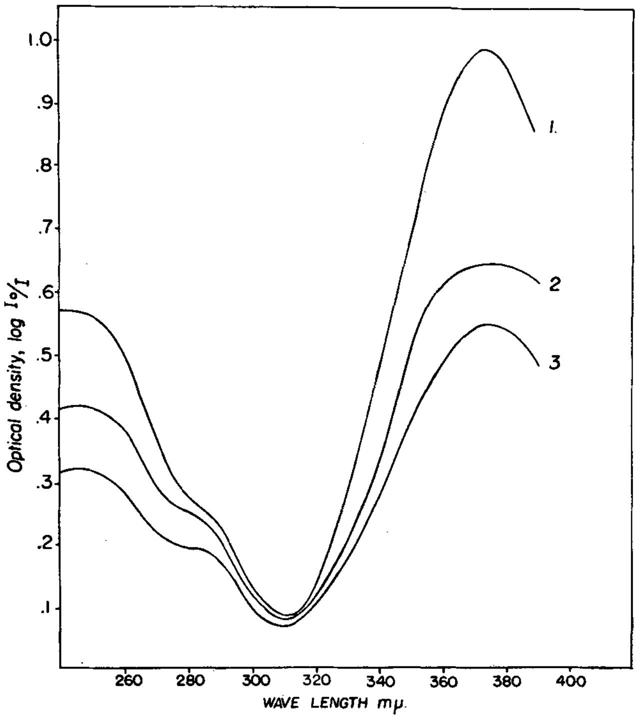

FIG. 3. Ultraviolet absorption spectra in ethanol.
1. S.N. 1-2H-128
2. S.N. 2-2H-135
3. 2,6-Decadienal DNPH

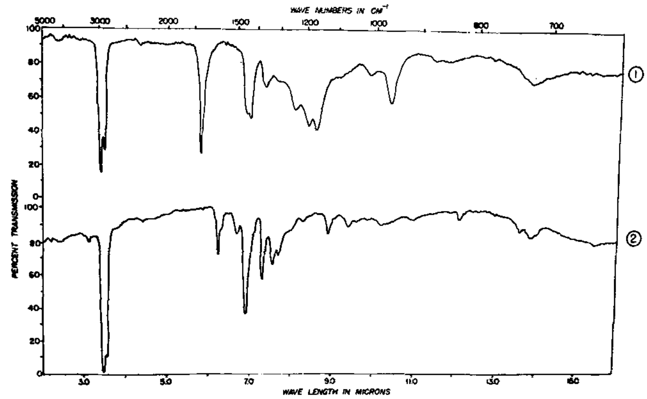

FIG. 4. Infrared absorption spectra.
1. S.N. 1-2H-99
2. S.N. 1-2H-128

The melting points of the dinitrophenylhydrazone derivative of some α,β-unsaturated straight chain aldehydes have been recorded as follows: 2-undecenal, 122.6°C. (24); 2-decenal, 128.8°C. (14); and 2-nonenal, 126°C. (25). This suggests that the isolated derivative may have been prepared from an unsaturated ketone. The negative reaction of the unfractionated ether-soluble fraction with iodine in alkaline

TABLE III

Comparison of Some Dinitrophenylhydrazone Derivatives of the Ether-Soluble Residue Neutral Fraction

Compound	M.P. (°C.)	Mixed M.P. (°C.)	Color	Wavelength of Max. Absorption (mμ)	Formula of Hydrazone	Elemental Analyses (Percentage)			
						C	H	N	Data
S.N. 1-2H-128	94.3- 95.0		red	376-77	$C_{16}H_{20}N_4O_4$	57.43	5.85	17.08	Found
S.N. 3-2H-128	5.0- 6.8		red-orange		$C_{38}H_{60}N_4O_4$	60.21	8.02	7.51	Found
S.N. 2-2H-136	132.5-133.2	133.8-134.5	orange	376-77	$C_{16}H_{20}N_4O_4$	57.89	5.79	17.97	Found
					$C_{16}H_{20}N_4O_4$	57.80	6.02	16.88	Calcd.
2,6-Decadienal DNPH	134.2-134.8		orange	376-77	$C_{16}H_{20}N_4O_4$	57.87	5.88	16.91	Found

potassium iodide further indicates that the carbonyl compound was not a methyl ketone.

2. *Compound S.N. 3-2H-128.* After rechromatographing several times followed by crystallization from ethanol, there were obtained 11.5 mg. of a red-orange semi-crystalline material with a m.p. of 5.0°-6.8°C. This compound appears to be a definite hydrazone derivative even though it is an oil at room temperature. An additional pass through the chromatographic column did not appear to raise the melting point (5.0°-6.9°C.) or even narrow the range.

A sample was submitted for elemental analyses and showed: C, 60.21; H, 8.02; N, 7.51. This product was apparently either not pure, in which case it may be a mixture of difficultly separable material or else it may be a polymerized or condensation product resulting from the autoxidation, for a calculation of the formula of the hydrazone derivative gave $C_{38}H_{60}N_4O_4$ or $C_{32}H_{56}O_8$ for the carbonyl compound.

3. *Compound S.N. 2-2H-136.* This material, after recrystallization from ethanol, was an orange crystalline product, yield 14 mg., m.p. 132.5°-133.2°C. It was rechromatographed several times, but this did not further raise the melting point.

An elemental analysis showed: C, 57.89; H, 5.79; N, 17.97. The empirical formula for the derivative calculated as $C_{16}H_{20}C_4N_4$ of $C_{10}H_{16}O$ for the original carbonyl compound. A mixed melting point with the 2,4-dinitrophenylhydrazone of 2,6-decadienal (m.p. 134.2°-134.8°C.) was 133.8°-134.5°C.

The ultraviolet and infrared absorption spectra of Compound S.N. 2-2H-136 and the 2,4-dinitrophenylhydrazone of 2,6-decadienal are shown in Figures 3 and 5, respectively. The ultraviolet absorption spectrum in ethanol showed a maximum at 376-77 mμ, characteristic of aliphatic α,β-unsaturated 2,4-dinitrophenylhydrazones (23).

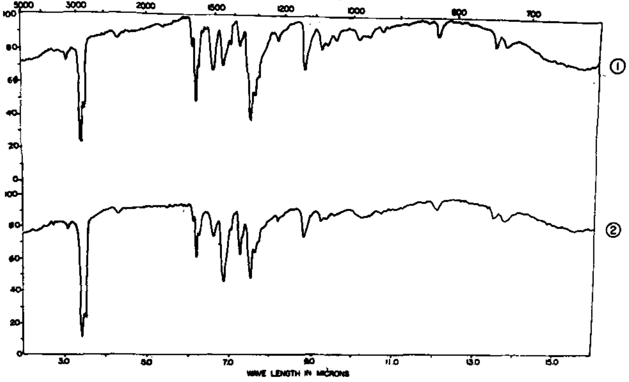

FIG. 5. Infrared absorption spectra in Nujol mull.
1. S.N. 2-2H-136
2. 2,6-Decadienal DNPH

Synthetic 2,6-decadienal was prepared by condensing 4-octenal, obtained by the method of Jacobson (24) from dihydropyran, with malonic acid according to the procedure of Galat to yield 2,6-decadienoic acid, b.p. 128°-130°C./1.5 mm.; m.p. 35°C.; neutralization equivalent 168.8 (theoretical neutral equivalent 168.2). Methyl 2,6-decadienoate, [b.p. 90°-95°C./2.5 mm.; N_D^{25} 1.4568; saponification equivalent 182.8 (theoretical 182.2)] obtained by the acid-catalyzed esterification of the acid was converted (21) with lithium aluminum hydride to give 2,6-decadienol, b.p. 68°-72°C./1.0 mm.; N_D^{25} 1.4608; d_{20}^{20} 0.906. Analysis: calcd. for $C_{10}H_{18}O$; C, 77.81; H, 11.69; found: C, 76.90; H, 11.46. The 2,6-decadienol was oxidized by the low temperature procedure of Delaby and Guillot-Allegre (22) to give 2,6-decadienal, b.p. 63°-70°/1.0 mm.; N_D^{25} 1.4595; d_{20}^{20} 0.844. Analysis: calcd. for $C_{10}H_{16}O$: C, 78.85; H, 10.52; found: C, 78.40; H, 11.44.

The semicarbazone (m.p. 161.0°-162.4°C.) and the 2,4-dinitrophenylhydrazone (m.p. 134.2°-134.8°C.) derivatives were prepared. The ultraviolet and infrared absorption spectra of the 2,4-dinitrophenylhydrazone of 2,6-decadienal were determined and are shown in Figures 3 and 5 respectively. The ultraviolet absorption spectrum in ethanol showed a maximum at 376-77 mμ.

A comparison of the elemental analyses together with some of the physical properties of Compounds S.N. 2-2H-136, S.N. 1-2H-128, and S.N. 3-2H-128 may be found in Table III.

Discussion

Methyl isolinoleate, prepared in a manner similar to that used in this investigation and isolated by a low temperature fractional crystallization procedure, has been shown to consist largely of 9,15- and 10,14- together with some 8,14-isolinoleic acids (24). While solvent crystallization of the methyl esters at low temperatures has been used to obtain highly purified linoleic acid, it was not possible to remove last traces of octadecenoic and conjugable dienoic esters by this procedure from the 95% isolinoleic acid concentrate. The present investigation confirms the previous work of both Lemon (9-12) and Rebello and Daubert (24) in that at least one of the double bonds of isolinoleic acid and possibly both have a trans—configuration for the infrared spectrum of the methyl isolinoleate (Figure 4) has a strong absorption peak at 10.3 microns.

It may be shown by the repeated reversion and deodorization of soybean oil, with no apparent decrease in its tendency to revert, that the precursors of reversion products must be present in much higher concentration than the flavor-producing substances (25). The yield of reversion products per each reversion and deodorization of the isolinoleate was 100 times that obtained from unhydrogenated soybean oil (3) and 17 times the quantity from partially hydrogenated soybean oil (19). Alkaline fractionation of the ether-soluble volatile and residue fractions of the autoxidation products were relatively effective operations as shown by the organoleptic and qualitative chemical analyses. The characteristic reversion-like flavor of the original deodorized product was found largely in the neutral fractions while the acid fractions had a sharp burnt-like odor (3).

Various saturated and unsaturated carbonyl compounds similar to those isolated in this work have been reported present in the off-flavor products of reverted oils. Hexanal, 2-octenal, and 2,4-decadienal have been isolated from autoxidized cottonseed oil (6), and 2-pentenal, 2-heptenal, hexanal, acetaldehyde, propionaldehyde, n-propyl ketone,and 2,4-decadienal have been reported present in reverted soybean oils (3, 4, 7, 19). Nye and Spoehr (28) have also found 2-hexenal in a leaf extract and attributed part of the grassy-like flavor to this compound. It was not unusual therefore to find compounds of this type, such as 2-hexenal and propionaldehyde, among the autoxidation products of methyl isolinoleate. The presence of a 2,6-decadienal however was unexpected for generally only the conjugated dienals have been isolated from reverted oils. According to present concepts (29, 30) of the mechanism of oxidation though, these are entirely possible decomposition products of the fatty acid hydroperoxides resulting from oxidative attack on the double bond activated α-methylene carbon atom. It has also recently been reported by Sharp *et al.* (31) that the further autoxidation of di-n-propyl ketone yields appreciable quantities of propionaldehyde.

The formation and isolation of acetone from the autoxidation of the isolinoleate may be somewhat questionable particularly in view of the negative reaction of the ether-soluble fraction with iodine in alkaline potassium iodide. Although only what were considered to be carbonyl-free solvents were used in the reversion, isolation, and identification portions of this work, it may have been introduced as a contaminant in one of the later stages.

On the basis of elemental analyses, color reactions, absorption spectra, and a consideration of previously characterized compounds, one of the unidentified derivatives was believed to be the dinitrophenylhydrazone of an α,β-unsaturated ketone. The presence of an α,β-unsaturated nine carbon straight chain ketone in the volatile fraction of autoxidized milk fat has been reported by Keeney and Doan (25). They have prepared the dinitrophenylhydrazone of 3-decene-5-one, m.p. 107°C., which leaves then one of the remaining five isomeric 10-carbon α,β-unsaturated ketones as a possible structure for this unknown compound.

Summary

Methyl isolinoleate has been prepared by the partial catalytic hydrogenation of a highly purified methyl linolenate obtained from linolenic acid which has been purified by bromination-debromination procedures.

After concentration by a low temperature fractional crystallization procedure from methanol, the crude material was molecularly distilled to give a product which analyzed 94.8% methyl isolinoleate and contained less than 0.5% methyl linolenate and 1.5% methyl linoleate.

The reversion of methyl isolinoleate has been shown to yield a mixture of off-flavor products which has a strong odor similar to that of reverted soybean oil.

From the autoxidation products there were isolated the 2,4-dinitrophenylhydrazone derivatives of six compounds. The chemical and physical properties of four of these derivatives were in close agreement with those of the corresponding dinitrophenylhydrazones of 2-hexenal, 2,6-decadienal, propionaldehyde, and acetone. One of the remaining compounds was believed to be the dinitrophenylhydrazone of an α,β-unsaturated ketone.

The isolation of derivatives of saturated and unsaturated carbonyls from the autoxidation products of methyl isolinoleate together with the relatively large yield of off-flavor materials compared to those obtained from partially hydrogenated and unhydrogenated soybean oil indicates that isolinoleic acid may be one of the precursors of reversion compounds.

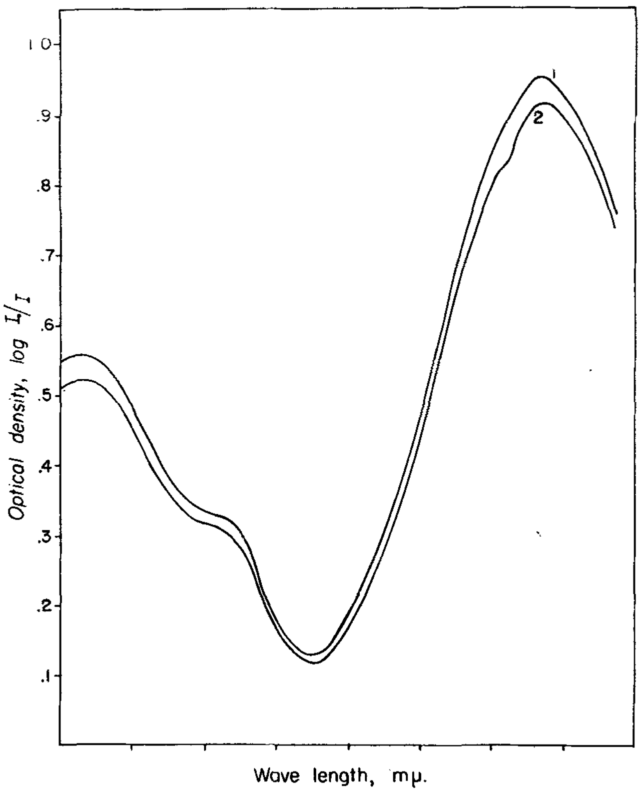

FIG. 6. Ultraviolet absorption spectra in ethanol.
1. S.N. 1-2H-108.
2. 2-Hexenal DNPH

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The Infrared Spectra and the Structural Relationships Between Alpha- and Beta-Eleostearic Acids and Their Maleic Anhydride Adducts

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RECENTLY Paschke, Tolberg, and Wheeler (15) have reviewed the subject of the cis, trans isomerism in the eleostearate isomers. They have pointed out that the previously proposed structures for the alpha- and beta-eleostearic acids have not been established definitely. These authors have adduced evidence from infrared spectra and chemical reactivities to show that alpha-eleostearic acid contains a cis, trans, trans conjugated triene system and that beta-eleostearic acid is the all trans isomer. Previously Morrell and co-workers (9, 11) as well as Chin (2), while investigating the maleic anhydride adducts of these two acids, reported that addition occurred across the 11 and 13 double bonds of alpha-eleostearic acid and across only the 9 and 11 double bonds of beta-eleostearic acid. Although their interpretation of these results led them to agreement regarding the cis, trans configuration of the alpha isomer, their views were divergent with regard to the beta isomer. If the beta-eleostearic acid is in fact an all trans isomer, as proposed by Paschke *et al.* (15), then two adducts would be predicted rather than only one. It is the purpose of this paper to present evidence for the existence of two maleic anhydride adducts of beta-eleostearic acid and to verify the structures of alpha- and beta-eleostearic acids through interpretation of data obtained by infrared spectroscopy as well as chemical means.

Experimental

Alpha- and beta-eleostearic acids. These acids were prepared from fresh authentic samples of tung oil according to the methods described by O'Connor *et al.* (13). The spectral analysis (13) showed that the alpha-acid (m.p. 48.0°C.) had a purity of 98.6% and that the beta-acid (m.p. 71°C.) was 96.4% pure. These acids had hydrogen-iodine values (14) of 271.8 and 270.9, respectively.

Maleinization. Ten percent solutions of alpha-and beta-eleostearic acids in toluene were refluxed with 150% excess of maleic anhydride until the characteristic yellow color had disappeared. The reaction mixtures were then diluted with an equal volume of ethyl ether and washed with water until free of maleic anhydride. Following drying and the removal of the solvents under reduced pressure, the recovered adducts were crystallized from 90% methanol solution. The alpha-eleostearic acid-maleic anhydride adduct, m.p. 64°C., analyzed 70.26% C and 8.67% H, calculated 70.18% C and 8.57% H, and had a hydrogen-iodine value of 132.2, calculated hydrogen-iodine value, 134.1. The beta-eleostearic acid-maleic anhydride addition product, m.p. 77°C., analyzed 70.25% C and 8.59% H, and had a hydrogen-iodine value of 131.8.

Hydrogenation of maleinated products. Approximately 2.5% solutions of the recrystallized maleinated products in glacial acetic acid were hydrogenated at room temperature and atmospheric pressure using an excess of platinum oxide catalyst. After the absorption of the theoretical amount of hydrogen (2 moles/mole) these products were freed of catalyst and solvent in the usual manner and finally dried in vacuo over solid sodium hydroxide. The white hydrogenation products for the alpha- and beta-isomers melted at 74°C. and 58°C., respectively. Morrell and Davis report 74°C. and 63°C., respectively (9).

Epoxidation of the maleinated products. Preliminary experiments were conducted on the alpha- and beta-maleinated products to determine if there was a possibillity of selective epoxidation of the cyclic or exocyclic double bonds. Then 3.7 grams of each of the recrystallized adducts were dissolved in 50 ml. of .4078 N perbenzoic acid-chloroform solution (approximate 10% excess based upon the epoxidation of two double bonds). After standing at 0°C. for 21 hours, titration of the excess perbenzoic acid indicated that 1.03 double bonds had been saturated. There was a white copious precipitate found in the reaction flask containing the beta-isomer, but there was no indication of an insoluble product formed in the reaction mixture containing the alpha-isomer. Infrared as well as chemical data presented elsewhere in this paper

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