step must await further studies with a peroxide-free substrate.

Metal ions of the first transition series may also act to terminate the free radical chain by forming complexes with one or more peroxy radicals, ROO·, giving rise to molecular decomposition products. Ingold (6) has reviewed this subject extensively citing investigations both in the autoxidation of fats and of other types of organic substrates. Chain termination is associated primarily with the lower oxidation state of a metal ion. This may explain the decreased pro-oxidative effect when histidine and 1 ppm of cobaltous ion (Co^{++}) were both present in the linoleate emulsion. Cobalt (present as the free ion or as a histidine complex) may form chain-terminating, nonradical decomposition products when it reacts with peroxy radicals and thus appears to inhibit the pro-oxidative action of histidine. By the same reasoning, transition metal ions which in our present investigation appear to have had little pro-oxidative interaction with histidine, may as chelates actually exist in a dynamic balance acting both as pro-oxidants and free radical chain-terminators. The shift in this balance would then depend on the electronic configuration of the d-shell and the nature of the chelating ligand.

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1-Octen-3-ol and Its Relation to Other Oxidative Cleavage Products from Esters of Linoleic Acid

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Abstract

By means of preparative GLC, 1-octen-3-ol and 2-*trans*-heptenal could be isolated from mildly oxidized linoleic acid ester and from oils containing this acid (e.g., soybean oil). A hypothesis for the origin of these two substances in natural products is given. The absence of 2-*trans*-octenal in the cleavage products from methyl linoleate, its presence in oils and the controversial experimental results obtained by various investigators, seem to be reconcilable by assuming the formation of an acetal. The suggested acetal may, on intermolecular cyclic rearrangement and cleavage, give 1-octen-3-ol.

Introduction

SOME characteristic aldehydes isolated from oxidative cleavage products of soybean oil have previously been identified (1,2). In the same material the secondary aliphatic alcohol, 1-octen-3-ol (vinyl amyl carbinol) was found. This alcohol, known as Matsutake alcohol, was first isolated from a Japanese mushroom by Murahashi (3) in 1938. Later, its presence was also observed in various kinds of mint and lavender oil (4,5,6). We found 1-octen-3-ol to be present also, in reverted linseed and rapeseed oils, and in oxidized palm oil.

Due to the partial structural similarity between 1-octen-3-ol and 13-hydroperoxy-9,11-octadecadienoate, it was supposed that linoleic acid was the precursor of this octenol. Therefore model autoxidation experiments were carried out with methyl linoleate. The results confirmed this expectation, not only for 1-octen-3-ol but for 2-*trans*-heptenal, which was also identified. 2-*Trans*-octenal, however, could not be isolated from the cleavage products, although it was detected in oils containing autoxidized linoleic acid, in accord with the results obtained by various investigators.

The isolation of 1-octen-3-ol from autoxidized methyl linoleate and from autoxidized oils, its identification and relationship with the aldehydes mentioned, are described below.

Isolation and Identification

Oxidative cleavage products of soybean oil obtained as previously described (1), were fractionated by means of gas/liquid chromatography (GLC). A fraction with characteristic "brown bean" and slight "mushroom" odor was isolated (Fraction 2 in Table I and peak 2 in Fig. 1).

TABLE I

Rt-Values, Odors, and Isolated Components of the GLC-Fractions of Neutral Volatile Cleavage Products from Oxidized Soybean Oil (up to C_9-Saturated Aldehyde)

Fraction No.	Rt at 93C (min)	Odor description	Identified as
1	6	Green beans	3-*cis*-hexenal + hexanal +3 *trans*-hexenal (1)
2	20	Brown beans + mushroom	2-*trans*-heptenal + 1-octen-3-ol + unknown substances
3	29	Rotten apples	2-*trans*-4-*cis*-heptadienal (2)
4	33	Rancid hazelnut	2-*trans*-4-*trans*-heptadienal (2)
5	42	Brown beans	2-*trans*-octenal + unknown substances
6	53	Citrus fruits	nonanal + unknown substances

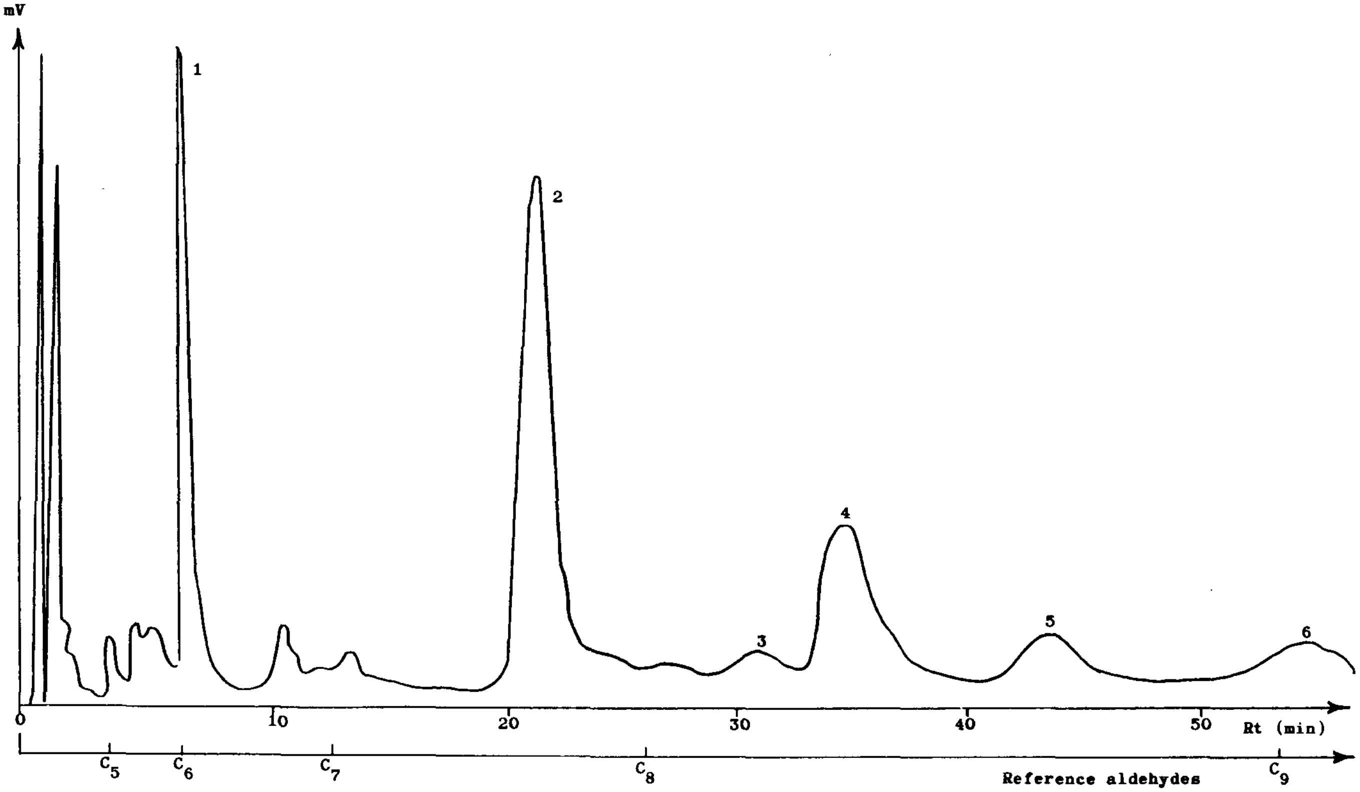

FIG. 1. GLC of soybean oil decomposition products. Analytical column: length 900 mm, non-polar immobile phase. Temperature 93C; gas pressure 24.5 cm Hg; gas rate 20 ml/min. For reference, the retention times of a homologous series of saturated aliphatic aldehydes are given on a second abscissa.

IR-analysis of Fraction 2 revealed the presence of at least three characteristic functional groups: an aldehydic, an alcoholic, and an ethylenic group.

After treatment of this fraction with acidic 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone (DNPH) of 2-*trans*-heptenal could be detected on the nitromethane/silicagel partition column. This aldehyde had already been found in reverted soybean oil in previous research (7). On the GLC column (non-polar immobile phase: celite/silicone oil), the retention time (Rt) of fraction 2 was found to be identical with that of synthesized 2-*trans*-heptenal. The odors of both the isolated and the synthesized compound were characterized as brown-bean odor, al-

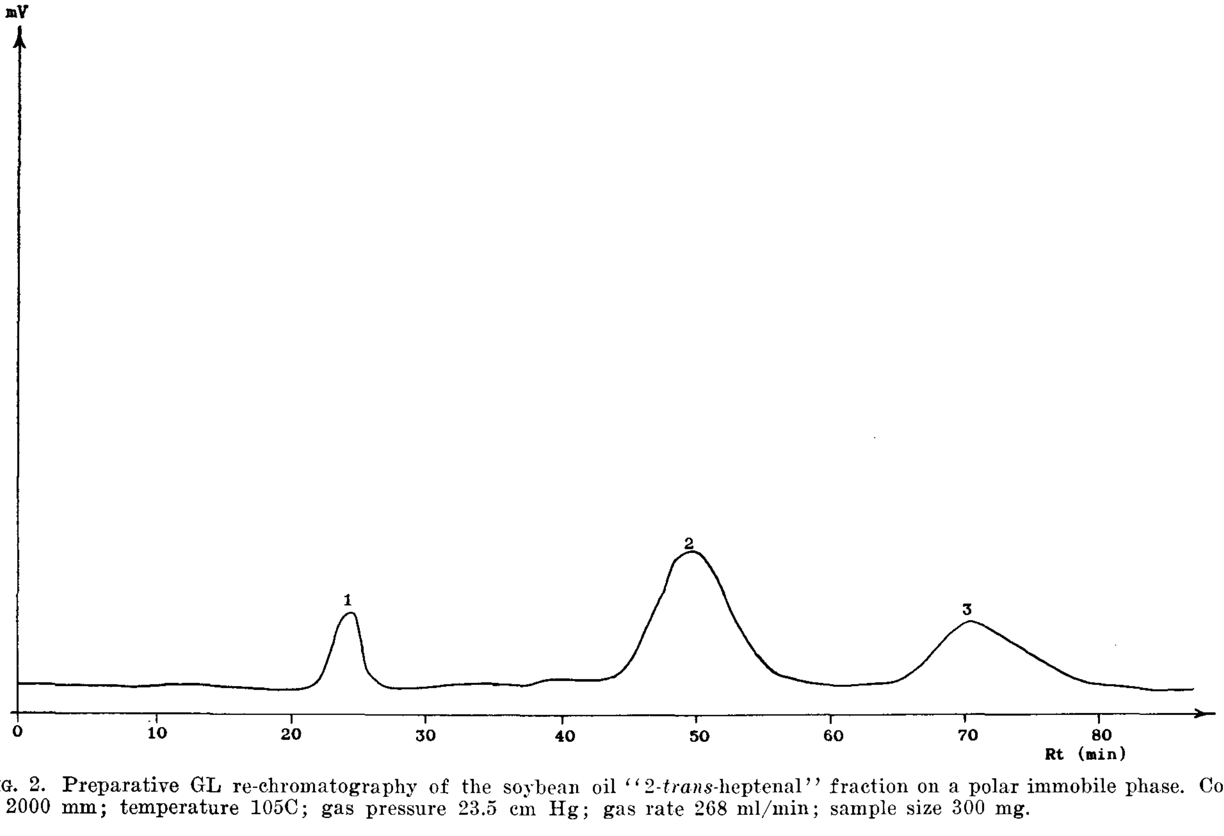

FIG. 2. Preparative GL re-chromatography of the soybean oil "2-*trans*-heptenal" fraction on a polar immobile phase. Column length 2000 mm; temperature 105C; gas pressure 23.5 cm Hg; gas rate 268 ml/min; sample size 300 mg.

though sometimes described as "cardboard" odor (8).

During earlier investigations (1958) of the cleavage products of oxidized palm oil, a GLC-fraction was isolated, which contained 2-*trans*-heptenal, but at the same time had a very pronounced mushroom odor. The corresponding GLC-fractions from oxidized linseed and rapeseed oil cleavage products also had both the brown-bean and the mushroom odor.

In an investigation into the nature of the fishy flavors of butterfat, Forss and co-workers (8) described a GLC-fraction, which contained, in addition to 2-*trans*-heptenal, a compound having mushroom odor.

A greater amount of Fraction 2 from soybean oil reversion products containing 2-*trans*-heptenal has now been isolated by means of preparative GLC. On using a non-polar and a polar immobile phase successively, this fraction could be split into at least three sub-fractions represented (Fig. 2) by:

Sub peak 1. This fraction (2–10%) having chocolate odor has not yet been identified. Mass-spectrometry (MS) indicates a mol wt of 138. Further identification is being attempted.

Sub peak 2. This fraction (65–70%) has been identified as 2-*trans*-heptenal (brown-bean odor). The mol wt, determined by MS, is 112.

Sub peak 3. This fraction (25–30%), having mushroom odor has been identified by means of IR-analysis (Table II, column 2) as a secondary alcohol with conjugated, terminal (vinylic) double bonds and with $(CH_2)_4$ skeletal vibration. By comparing the IR-spectrum and the gas/liquid chromatogram on polar and non-polar immobile phases with those of synthesized 1-octen-3-ol (Table II, column 3), and by determining the mol wt by MS (128), the identity of the isolated and the synthesized compound could be proved.

As mentioned before, the most probable precursor of 1-octen-3-ol is linoleic acid. To confirm this, methyl linoleate (purity ca. 98%), prepared from safflower oil by means of urea adduct, was autoxidized at room temperature to peroxide values (POV) of 8 and 80. After a mild thermal decomposition, the ester was degassed in high vacuum. The volatile cleavage products were first chromatographed on a non-polar immobile phase (see Table III and Figs. 3a, 3b).

TABLE II

IR-Absorption Maxima (cm^{-1}) of Isolated and Synthesized 1-Octen-3-ol

Type of vibration	Isolated	Synthesized
$-(CH_2)_4$ skeletal vibration	m 725	m 725
$-CH_2$ out-of-plane deform. vibr	s 912	s 915
$=CH$ out-of-plane deform. vibr	s 999	s 990
C—O stretching vibr. and OH deform. vibr	s,m 1024	s,m 1020
CH in-plane deform. freq	s,w 1280-1340	s,w 1290-1340
CH_3 symm. deform. vibr	m 1382	m 1380
CH_2 in-plane deform	m 1425	m 1425
CH_2 asymm. deform. vibr	s 1465	s 1465
C=C stretching vibr	m 1648	m 1642
Overtone band	m 1725	m 1740
Overtone band of 915 cm^{-1}	m 1842	m 1835
CH stretching freq. of CH_2/CH_3	s 2860 s 2925	s 2845 s 2920
CH stretching of $CH=CH_2$	m 3075	m 3075
OH stretching vibr	s 3360	s 3350

s = strong, m = medium, w = weak.

The 2-*trans*-heptenal fraction (Table III, peak 8 and Figs. 3a, 3b), fractionated on a preparative GLC-column, was then collected and rechromatographed on a second one with a polar immobile phase. Two fractions (represented in Fig. 4 by two sub peaks a and b) were isolated, which had the same analytical and odor characteristics as synthetic 2-*trans*-heptenal (a) and 1-octen-3-ol (b). This result strongly supports the assumption that linoleic acid is indeed the precursor of these compounds. It should be noted that in these model experiments no 2-*trans*-octenal could be detected.

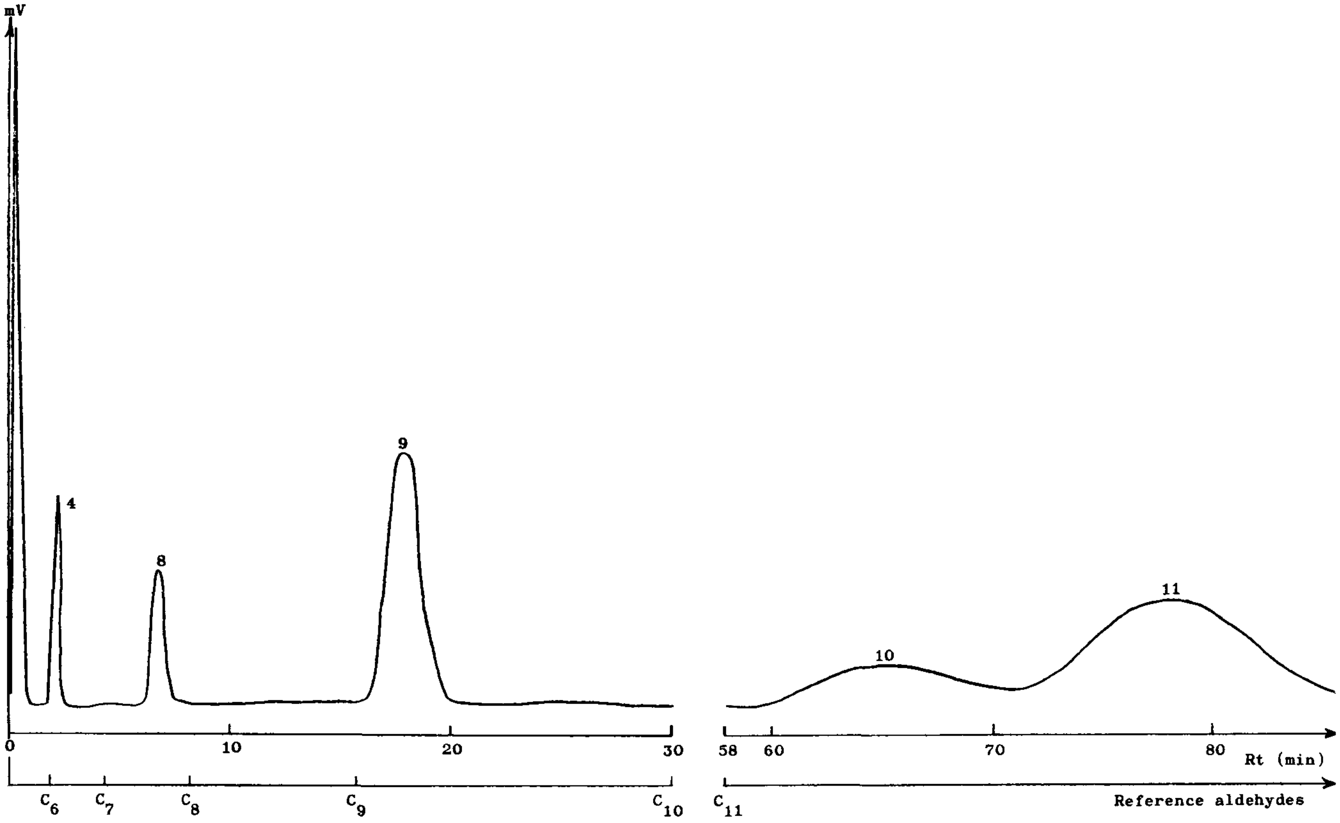

Fig. 3a. GLC of volatile decomposition products from methyl linoleate autoxidized to POV 8. Temperature 100C; gas pressure 51 cm Hg; gas rate 77 ml/min; non-polar immobile phase.

Experimental

A. *Methods*

The nitrogen stripping of pre-oxidized or reverted oils, the purification of collected volatile decomposition products, infrared and UV analyses, the preparation of DNPHs, and partition chromatography of DNPHs on the nitromethane/silicagel column and on paper are described in previous papers (1,2). Mass-spectrometric analyses were made with a Metropolitan-Vickers MS 2 analyzer. GLC-separations were performed in glass columns (length 900 mm; diameter 4 mm) with a gas-density balance as detector.

To collect greater amounts of a fraction (sample input 100–300 mg) preparative GLC was carried out in straight glass columns (length 1300 mm; diameter 10 mm) and in U-shaped glass columns (length 2000 mm; diameter 15 mm). The non-polar immobile phase was celite/silicone oil (30%), the polar phase celite/poly-ethyleneglycol adipate (30%). The detector was either a gas-density balance or a shunted katharometer. The mobile phase was purified nitrogen freed from oxygen by a catalytic BTS[1]-unit. The column was thermostatted. The effluent fractions were trapped in U-shaped capillaries or in spiral condensers cooled in liquid nitrogen. The further conditions are given under the relevant figures (Figs. 1–4).

The preparation of the methyl ester of linoleic acid was carried out in four steps by means of urea-fractionation of safflower oil fatty acids in methanolic solution. The fatty acid composition of the linoleate is shown in Table IV.

Autoxidation of methyl linoleate to peroxide values 8 and 80 was achieved by allowing it to stand in a wide beaker for various times at room temperature.

TABLE III
Rt-Values and Isolated Components of the GLC-Fractions of Volatile Cleavage Products of Oxidized Methyl Linoleate (POV 8 and 80)

Fraction No. in		Rt (min)		Rel. quant. estimated from Fig. 3a (%)	Remarks
Fig. 3a (POV 8)	Fig. 3b (POV 80)	At 100C (POV 8)	At 82C (POV 80)		
....	1	....	2.0	....	Unidentified
....	2	....	3.5	....	Pentanal
....	3	....	5.0 (sh)	....	Hexanal+unknown substances
4	4	2.0	7.0 (sh)	~ 5	Unidentified
....	5	....	11.5 (sh)	....	Unidentified
....	6	....	15	....	Unidentified
....	7	....	18	....	Unidentified
8	8	6.5	28	~ 5	2-*Trans*-heptenal + 1-octen-3-ol
9	9	16.5	82	~35	By IR analysis: C-O-C group
10	....	60.0	....	~15	2-*Trans*-4-*cis*-decadienal
11	....	70.0	....	~40	2-*Trans*-4-*trans*-decadienal

sh = shoulder.

Degassing after mild thermal decomposition (30 min at 150C) was carried out in high vacuum, as described by de Bruyn and Schogt (9). Degassing temperature: 80C in case of POV 8; 40C in case of POV 80. Degassing period: 4 h. A cooled spiral capillary unit was used to condense and collect the volatiles.

TABLE IV
GLC-Analysis of Methyl Linoleate

Fatty acid	"Linoleic acid" methyl ester (%)
C_{16} saturated	Traces
C_{16} mono-unsaturated	0.4
C_{18} saturated	......
C_{18} mono-unsaturated	2.2
C_{18} di-unsaturated	97.4
C_{20} mono-unsaturated	Traces

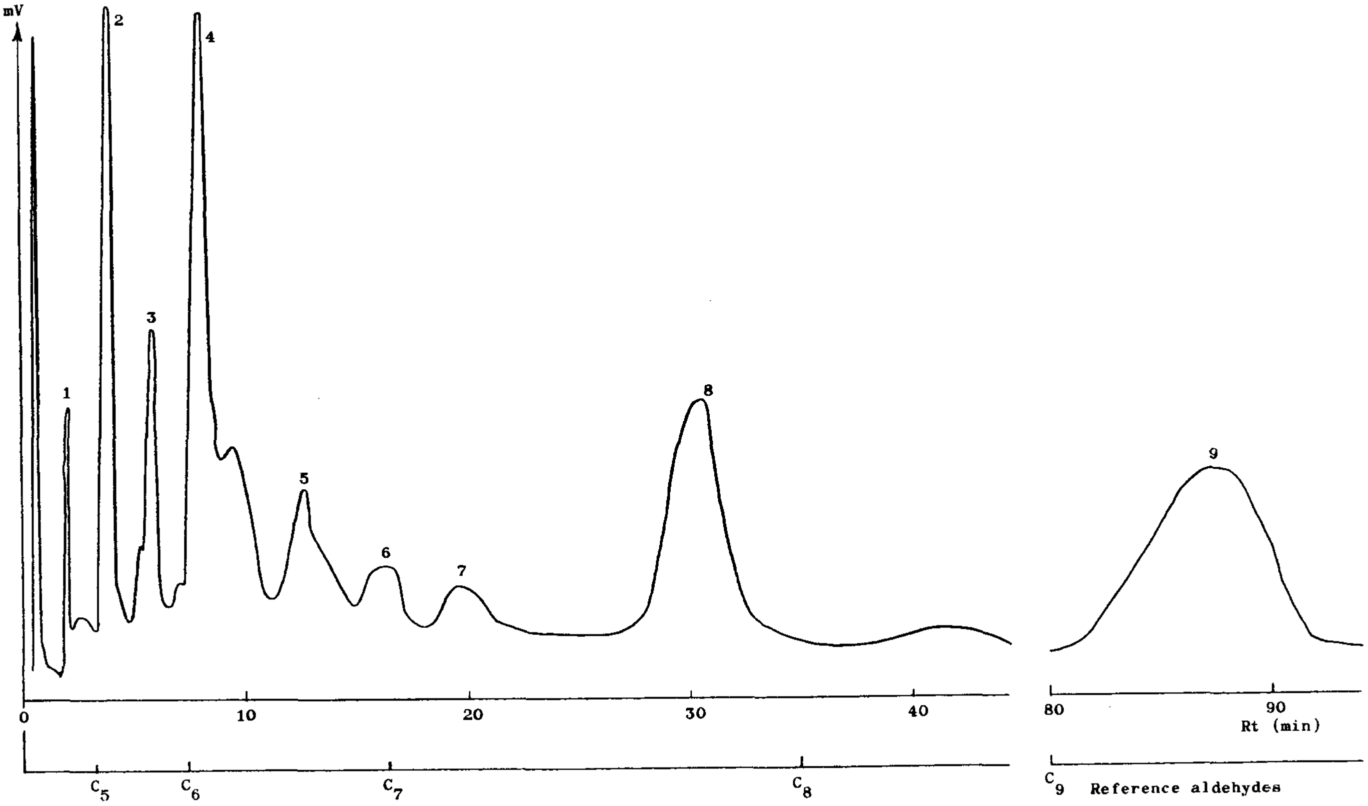

FIG. 3b. GLC of volatile decomposition products from methyl linoleate autoxidized to POV 80. Temperature 82C; gas pressure 50 cm Hg; gas rate 230 ml/min; non-polar immobile phase.

For both figures, the retention times of the series of saturatedaldehydes are given on a second abscissa.

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[1] BTS-catalyst of BASF, Ludwigshafen, Western Germany DBP 869,052 and 965,634.

B. *Synthesis of Model Substances*

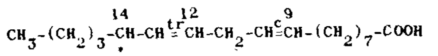
2-*Trans*-heptenal was prepared by Doebner's method from pentanal and malonic acid as well as by Radlove's method (10) via α-bromo-heptanal.[2] 1-Octen-3-ol was synthesized by reacting 1 mole acrolein with 1 mole amyl magnesium bromide, as described by Levene and Walti (11).

Discussion

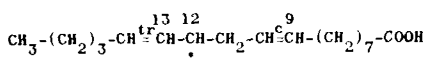
2-Trans-Heptenal. Daubert and co-workers (7) reported the presence of 2-*trans*-heptenal in soybean oil and assumed it to be an oxidative cleavage product of a conjugated trienoic acid. In model experiments with linoleic acid Lathlean (12) found that hexanal and possibly 2-*trans*-heptenal and pentanal were present among the aldehydes after partial cleavage of this acid, whereas Ellis et al. (13) detected 2-*trans*-heptenal, hexanal, and 2,4-decadienal, as the chief cleavage products, and acetaldehyde, propanal, 2-*trans*-octenal, and 2-*trans*-nonenal as minor constituents. In our model experiments both with pure linoleate and with soybean oil cleavage products we detected 2-*trans*-heptenal as one of the minor constituents.

The following scheme may show how this aldehyde can be derived from linoleic acid. A linoleic acid radical (I) leads, via an allyl rearrangement, to radical (II). The hydroperoxide (III) can decompose to yield 2-*trans*-heptenal (IV) (fraction 8 in Table III, and peak 8 in Figs. 3a and 3b). The presence of pentanal (VI) as a possible cleavage product of 14-hydroperoxy-9-*cis*-12-*trans*-octadecadienoate (V) has also found experimental support (fraction 2 in Table III and peak 2 in Fig. 3b).

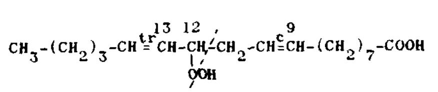
This proposed mechanism is not completely supported by the findings of Sephton and Sutton (14), who detected by oxidation of the various hydroxystearic acids, obtained by reduction of the corresponding hydroperoxy-octadecadienoates, a considerable amount of C_5- but only a small amount of C_4-monocarboxylic acids. These acids might partly originate from 14-hydroperoxy-octadecadienoate. If this is true, 12-hydroxy-octadecadienoate must also be found. This must lead to the formation of C_7- and C_6-monocarboxylic acids. Only the latter was found, which may probably be explained by the formation of only a min quantity of this 12-hydroperoxide, which might escape detection.



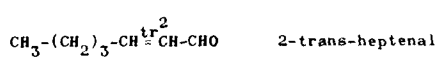
$\mathrm{CH_3\text{-}(CH_2)_3\text{-}\overset{14}{\underset{\bullet}{C}}H\text{-}CH\overset{tr}{=}\overset{12}{C}H\text{-}CH_2\text{-}CH\overset{c}{=}\overset{9}{C}H\text{-}(CH_2)_7\text{-}COOH}$ (I)



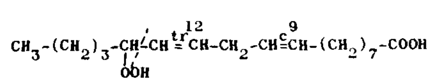
$\mathrm{CH_3\text{-}(CH_2)_3\text{-}CH\overset{tr}{=}\overset{13}{C}H\text{-}\underset{\bullet}{\overset{12}{C}}H\text{-}CH_2\text{-}CH\overset{c}{=}\overset{9}{C}H\text{-}(CH_2)_7\text{-}COOH}$ (II)



$\mathrm{CH_3\text{-}(CH_2)_3\text{-}CH\overset{tr}{=}\overset{13}{C}H\text{-}\underset{\underset{OOH}{|}}{\overset{12}{C}H}\text{-}CH_2\text{-}CH\overset{c}{=}\overset{9}{C}H\text{-}(CH_2)_7\text{-}COOH}$ (III)



$\mathrm{CH_3\text{-}(CH_2)_3\text{-}CH\overset{tr}{=}\overset{2}{C}H\text{-}CHO}$ 2-trans-heptenal (IV)



$\mathrm{CH_3\text{-}(CH_2)_3\text{-}\underset{\underset{OOH}{|}}{C}H\text{-}CH\overset{tr}{=}\overset{12}{C}H\text{-}CH_2\text{-}CH\overset{c}{=}\overset{9}{C}H\text{-}(CH_2)_7\text{-}COOH}$ (V)

$\mathrm{CH_3\text{-}(CH_2)_3\text{-}CHO}$ pentanal (VI)

tr = trans; c = cis

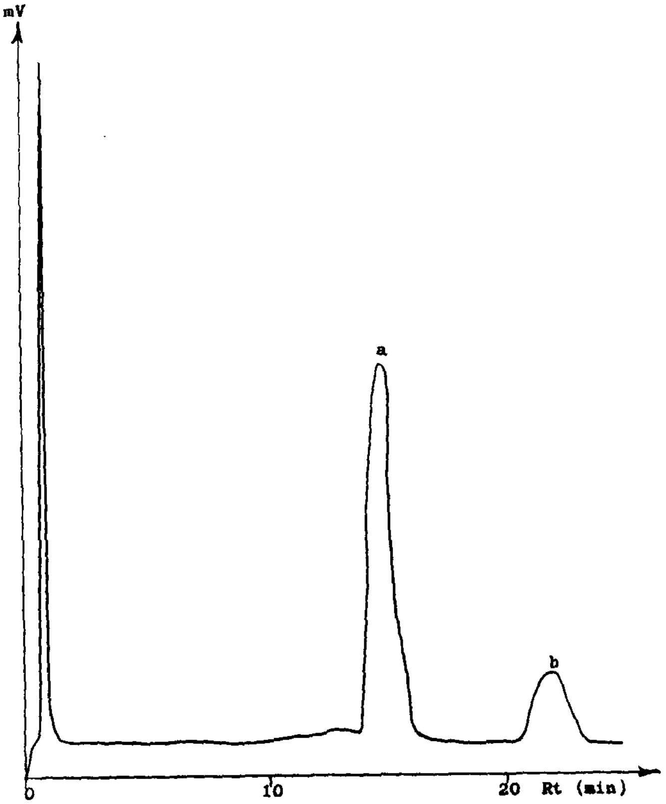


FIG. 4. Analytical GL re-chromatography of the "2-*trans*-heptenal" fraction from linoleate on a polar immobile phase. Temperature 80C; gas pressure 50 cm Hg; gas rate 70 ml/min.

2-Trans-Octenal. The experiments of Sephton and Sutton (14) gave no evidence for the presence of 11-hydroperoxy-octadecadienoate in measurable amounts (no C_7- and C_8-monocarboxylic acids were found) and were in complete agreement with the findings of Bergström (15) and Privett et al. (16). So on this ground only very small amounts of 2-*trans*-octenal may be expected in linoleic acid cleavage products.

Ellis et al. (13) and Badings (17) found evidence for 2-*trans*-octenal in their model experiments with linoleic acid. In analogous experiments Patton and co-workers (18), however, could not detect 2-*trans*-octenal. All these investigators identified this compound by various kinds of partition chromatography of the DNPHs, formed from the cleavage products. In our model experiments no detectable amount of 2-*trans*-octenal was present in the GLC-picture.

On the other hand Swift et al. (19) found, as their DNPHs, 2-*trans*-octenal, hexanal, and 2,4-decadienal, originally isolated as semicarbazones from cottonseed oil cleavage products. Also in our experiments with soybean oil a small amount of 2-*trans*-octenal was found in the GLC-picture (fraction 5 in Table I and peak 5 in Fig. 1).

Because this aldehyde has been found so often in oils containing linoleic acid, and since it is to be expected, according to Farmer's theory, from linoleic acid, it might be suggested that the absence of detectable amounts of 2-*trans*-octenal in some of the experiments would be balanced by the formation of 1-octen-3-ol.

This secondary alcohol may be oxidized to 2-*trans*-octenal, via an allyl rearrangement, but this depends on the reaction conditions.

1-Octen-3-ol. Whereas in soybean oil 1-octen-3-ol and 2-*trans*-octenal were found, in the linoleic acid

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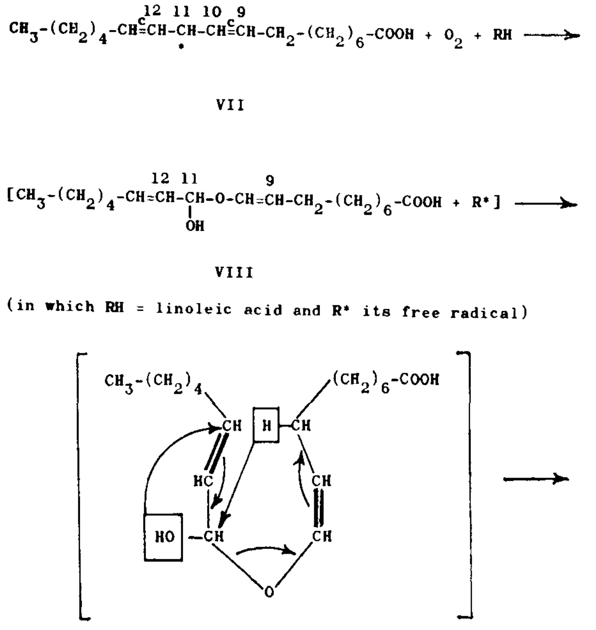
[2] The odor of the products obtained by both methods was identical to that of our product isolated from soybean oil.

model experiment no 2-*trans*-octenal was detectable. To explain the occurrence of 1-octen-3-ol, we postulate the formation of the hemi-acetal (VIII) from the unstable free radical of linoleic acid (VII) via an unstable intermediate. This hemi-acetal (VIII) could possibly undergo an intermolecular cyclic rearrangement (IX) and could be cleaved to a secondary unsaturated alcohol (by allylic rearrangement) e.g., 1-octen-3-ol (X) and an unsaturated aldehydic acid (XI), as postulated recently also by Frankel et al. (20).

The presence of acetal functions in oxidized oils and fats was postulated as early as 1923 [cf. Powick (21)].

Proposed reaction scheme:



$$CH_3\text{-}(CH_2)_4\text{-}CH\overset{c}{=}\overset{12}{C}H\text{-}\underset{\bullet}{\overset{11}{C}H}\text{-}\overset{10}{C}H\overset{c}{=}\overset{9}{C}H\text{-}CH_2\text{-}(CH_2)_6\text{-}COOH + O_2 + RH \longrightarrow$$

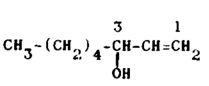
VII

$$[CH_3\text{-}(CH_2)_4\text{-}CH{=}\overset{12}{C}H\text{-}\underset{OH}{\overset{11}{C}H}\text{-}O\text{-}CH{=}\overset{9}{C}H\text{-}CH_2\text{-}(CH_2)_6\text{-}COOH + R^{*}] \longrightarrow$$

VIII

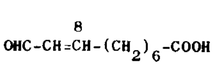
(in which RH = linoleic acid and R* its free radical)

IX



$$CH_3\text{-}(CH_2)_4\text{-}\underset{OH}{\overset{3}{C}H}\text{-}CH{=}\overset{1}{C}H_2$$

X



$$OHC\text{-}CH{=}\overset{8}{C}H\text{-}(CH_2)_6\text{-}COOH$$

XI

Some stabilizing interaction on the unstable free radical of linoleic acid (VII) by an unknown oil constituent may account for the presence of 2-*trans*-octenal in oils. In the absence of such a stabilizing constituent, 1-octen-3-ol will be formed, which can again secondarily be oxidized to 2-*trans*-octenal or other products.

Acknowledgment

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Freezing Point Behavior of the Ternary Reciprocal Salt Pair System Involving the Morpholine and 2,2'-Dipyridylamine Salts of Stearic and Palmitic Acids[1]

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Abstract

Binary and quasi-binary freezing point data have been obtained to establish the freezing point diagram for the ternary reciprocal salt pair system, involving the morpholine and 2,2'-dipyridylamine salts of stearic and palmitic acids. The diagram shows that there are six crystallization surfaces representing equilibrium with crystals of MS, MP, DS, DP, DS·DP, and MS·DP. The compositions and primary freezing points of the six peritectic and five eutectic mixtures have been determined. From the diagram it is possible to predict for any molten mixture of these four salts under equilibrium conditions the temperature at which crystals of each component will appear on cooling, the yields of these crystals and the composition of the liquid phase at various temperatures, and the temperature at which maximum yields of crystals of the specific salts can be obtained.

Introduction

IN THE COURSE of an investigation of the use of mixed amines in the separation and purification of long chain fatty acids (2), fundamental information

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