Isolation of Two Pairs of Isomeric 2,4-Alkadienals from Soybean Oil-Reversion Flavor Concentrate

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By means of gas-liquid chromatography two isomeric 2,4-hepta- and 2,4-decadienals have been isolated from volatile decomposition products of soybean oil. The stereoconfiguration of the isomers appeared to be 2t, 4c, and 2t,4t.

The precursor of the two heptadienals is assumed to be linolenic acid and that of the two decadienals, linoleic acid.

According to Farmer's (1) autoxidation theory, oils containing linoleic acid may give rise to the formation of three decomposition products: hexanal, 2-octenal, and 2,4-decadienal (2). The isolation of the latter from such oils or from linoleic acid esters is mentioned frequently in the literature (3-8).

The isolation of 2t,4c- and 2t,4t-decadienals from palm oil and peanut oil decomposition products, thus from oils containing only a single polyunsaturated acid, namely, linoleic acid, has been published earlier (9). The existence of these two isomers could be expected from stereochemical considerations (10) as well as from the autoxidation theory mentioned above.

On the other hand, von Pezold (11) isolated 2,4-heptadienal and/or 2,4-octadienal from reverted or oxidized soybean oil and concluded that these substances may be decomposition products of hydroperoxides of linolenic acid. No other configurational details about the chemical structure of these aldehydes have been reported.

In a recent publication (12) on volatile decomposition products of soybean oil the isolation of one of the main reversion products, 3-*cis*-hexenal, with a "green bean" flavor, has been reported. Linolenic acid was assumed to be the most probable precursor of this aldehyde.

In the course of the investigation 3-*trans*-hexenal, among other carbonyl derivatives, was also found. However the odor of this compound seemed to contribute practically nothing to the reversion flavor of soybean oil.

As soybean oil contains both linoleic and linolenic acids, it was expected that, apart from the two isomeric 2,4-decadienals, the two isomeric 2,4-heptadienals would also be present in the volatile soybean oil decomposition products.

The isolation of the two pairs of isomeric 2,4-alkadienals is described below.

Isolation and Identification of the Four 2,4-Alkadienals

Fractionation by gas liquid chromatography of the volatile soybean oil decomposition products, obtained in the manner previously described (12), resulted in the separation of four substances, each characterized by a peak in the chromatograms (Figures 1 and 2).

The Rt-values and odor characteristics are recorded in Table I.

The results of infrared analysis of the four substances collected are shown in the following table.

Earlier experience with the two isomeric decadienals enabled us to identify all four compounds as 2,4-alkadienals. Compounds 3 and 7 have the 2t, 4c-configuration (triplets at about 960, 990, 1015 cm^{-1} and 970–980, 993, 1018 cm.$^{-1}$, respectively), and compounds 4 and 8 the 2t, 4t-configuration (doublets at about 992, 1015 cm^{-1} and 991, 1013 cm^{-1}, respectively).

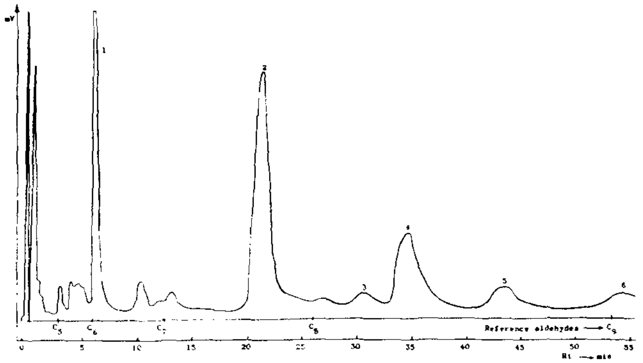


FIG. 1. *GLC of soybean oil decomposition products at 93°C.* Column: length 900 mm., diameter 4 mm.; carrier: Celite 545; immobile phase: silicone oil (30% Dow-Corning); mobile phase: nitrogen; gas pressure: 24.5 cm. Hg; gas rate: 29 ml./min. For reference purposes the retention times (Rt-values) of an homologous series of saturated aliphatic aldehydes are given on a second abscissa.

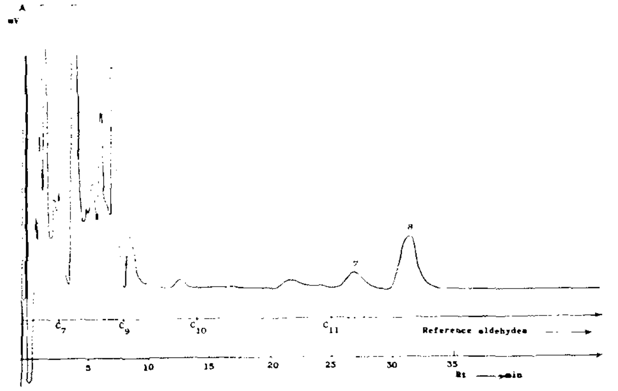


FIG. 2. *GLC of soybean oil decomposition products at 137° C.* Data of column, see Figure 1; gas pressure: 45.5 cm. Hg; gas rate: 45.5 ml./min. Second abscissa for reference aldehydes.

TABLE I
Rt-Values and Odors of the Relevant GLC-Fractions of Reverted Soybean Oil

Fraction number	Rt (min./°C.)	Odor	Remarks
3	29/93	Rotten apples	See Fig. 1
4	33/93	Rancid hazelnut	See Fig. 1
7	26/137	Sweet, aldehydic	See Fig. 2
8	30/137	Fatty aldehydic	See Fig. 2

The compounds corresponding with Peaks 7 and 8 were, in addition, identified by Rv values of their corresponding dinitrophenylhydrazones (DNPHs) on the nitromethane/silicagel partition column (12), ultraviolet data (λ_{max} values), and Rf-values by paper chromatography (12).

From these investigations it appeared that the above compounds were the two isomeric 2,4-deca-

TABLE II

IR Absorption Maxima (cm^{-1}) of the Four Isolated Compounds

Type of vibration	Peak 3	Peak 4	Peak 7	Peak 8
—$(CH_2)_4$ skeletal vibration	w 725		m 725 w 750	m 725
		w 810		w 840
	m sharp 860	m 860 m 875 m 920	m sharp 860	sh 875 w 920
=CH out-of-plane deform. vibr.	m 960 m sharp 990 m 1015	sh 965 s 992 s 1015	m,br 970—980 m sharp 993 m sharp 1018	s 991 s 1013
C—O vibr. of aldehyde	s 1120 s 1160	s 1125 s 1170	sharp 1123 sharp 1162	s 1120 s 1170
CH deform. freq	m 1385	s 1390	m 1380 w,sh 1440	s 1382
CH deform. freq	s 1470	s 1465	s 1470	s 1470
C=C conjugated (aliph.)	sh 1600 s 1630	m 1605 s 1645	sh 1600 s 1640	m 1603 s 1646
C=O stretch. vibr. of α-β, γ-δ unsat. aldehyde	s 1680	s 1690	s 1690	s 1695
CH—stretch. vibr. of aldehyde	m 2730	m 2750	m 2750	m 2750
CH—stretch. freq. from CH_2/CH_3	s 2870 s 2920 s 2970	2910 sh 2950 s 2995	s 2885 s 2960 sh 2980	s 2885 s 2960 sh 2980
—CH=stretching	sh 3020	sh 3040	sh 3030	sh 3030

w = weak; m = medium; s = strong; sh = shoulder; br = broad.

TABLE III

Partition Chromatography of the DNPHs Formed from Compounds 3, 4, 7, 8

Substance (DNPH)	Rv (ml.)[a]	Remarks
Peak 3 } Fig. 1	380	2t,4c-heptadienal
Peak 4	395	2t,4t-heptadienal
Peak 7 } Fig. 2	137	2t,4c-decadienal
Peak 8	150	2t,4t-decadienal
Reference DNPHs:		
2,4-heptadienal	400	t,t
2,4-octadienal	290	t,t
2,4-nonadienal	210	t,t
2,4-decadienal	155	t,t
2,4-hendecadienal	111	t,t

[a] All compounds have a λ_{max} in $CHCl_3$ of 303–6 and 387–390 mμ.

dienals. In the same way the compounds corresponding with Peaks 3 and 4 were found to be the two isomeric 2,4-heptadienals (Table III). Lack of $CH_2)_4$-skeletal vibration at 725 cm^{-1} and the close similarity of the spectra to those of the decadienals clearly point to these compounds.

Synthesis and Analysis of Model Substances

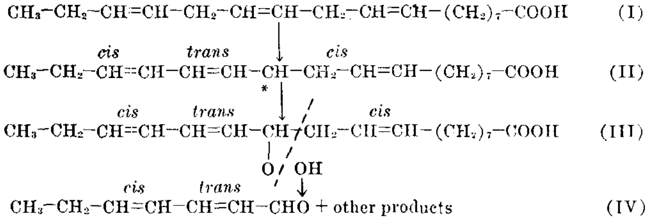
The synthesis of the 2t, 4t-hepta- and decadienals was achieved by applying Doebner's method, using propanal and n-hexanal as starting materials [cf. Forss and Hancox (13)].

For the synthesis of 2t, 4c-decadienal the correspounding decadienoic acid, isolated from Stillingia oil, was converted into the fatty acid chloride by using thionyl chloride. The fatty acid chloride was reduced with lithium-tert-butoxyaluminohydride in diethylene glycol-dimethyl ether [cf. method proposed by Brown and Subba Rao (14)].

2t, 4c-Heptadienal was not synthesized.

Discussion

The occurrence of the two isomeric 2,4-heptadienals in soybean oil decomposition products can be explained by Farmer's (1) autoxidation theory and the configuration rules of Nichols et al. (10), as applied to linolenic acid:



$$\overset{}{CH_3-CH_2-}\overset{cis\ 15}{CH=CH}-CH_2-\overset{cis\ 12}{CH=CH}-CH_2-\overset{cis\ 9}{CH=CH}-(CH_2)_7-COOH \qquad (I)$$

$$CH_3-CH_2-\overset{cis}{CH=CH}-\overset{trans}{CH=CH}-\underset{*}{CH}-CH_2-\overset{cis}{CH=CH}-(CH_2)_7-COOH \qquad (II)$$

$$CH_3-CH_2-\overset{cis}{CH=CH}-\overset{trans}{CH=CH}-\underset{\underset{O-OH}{|}}{CH}-CH_2-\overset{cis}{CH=CH}-(CH_2)_7-COOH \qquad (III)$$

$$CH_3-CH_2-\overset{cis}{CH=CH}-\overset{trans}{CH=CH}-CHO + \text{other products} \qquad (IV)$$

The abstraction of a hydrogen atom at carbon atom number 14 of linolenic acid (I) in the initial stage of oxidation can lead *via* an allylic rearrangement to radicals, such as mesomer (II). As a primary oxidation product, the hydroperoxide (III) is formed, which on decomposition may form 2t,4c-heptadienal (IV).

The 2t,4t-heptadienal will probably be the more stable isomer and can be formed either as a secondary reaction product during further rearrangement of the free radical of linolenic acid to 12-hydroperoxy-9c,13t,15t-octadecatrienoic acid or by isomerization of 2t,4c-heptadienal.

The two isomeric 2,4-decadienals may be derived analogously from linoleic acid, as has been shown in a previous paper (9).

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