

Keeping Properties of Edible Oils. III. Identity of Trace Materials Adsorbed from Peanut Oil by Chromatography on Alumina

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Abstract

A peanut oil of improved quality was obtained by replacing active earth bleaching in the refining process by treatment with alumina. To determine which components of the oil were removed and modified by this treatment, the material adsorbed on the alumina was examined. Off-flavor precursors were not concentrated, but chemical modification of precursors had taken place. Alumina treatment probably owes its effectiveness in part to removal of off-flavor precursors and pro-oxidants, and in part to suppression of undesirable side reactions which occur in bleaching earths. Hydroperoxides originally present in the oil were almost entirely destroyed on the alumina, and the adsorbate was found to be enriched in oxidized, hydroxylated, and unsaponifiable material. The presence of glycerides containing both saturated and α , β unsaturated (and possibly traces of α , β , γ , δ diunsaturated) aldehyde groups was demonstrated. The adsorbate also contained a considerable proportion of glycerides containing polar groups, e.g. hydroxyl, in the fatty acid radicals; the bulk of these appeared to be hydroxydienoic acid. Gas liquid chromatography (GLC) of the methyl esters of the fatty acids of the adsorbate was used to detect simple oxidized fatty acids such as keto, epoxy, and hydroxy acids. Adsorption on alumina may prove to be a powerful tool for the isolation of aldehydoglycerides and glycerides of hydroxy-acids from oils and fats.

Introduction

THE USE OF alumina in the refining of oils has been described in a previous paper (1). It was found that the quality of refined oils could be improved by replacing conventional bleaching with a new process in which a solution of the oil in petroleum ether was passed through a column of activated alumina. The improvement in oil quality suggests that precursors of off-flavors or pro-oxidants, which remain in the oil during normal bleaching, are removed by the alumina. The material removed by the alumina was extracted and examined to investigate the mechanism of the oil quality improvement.

The selected peanut oil was dissolved in petroleum ether (bp 40–60C) and then treated on a column of alumina, as described previously (1), to give a 94% yield of improved oil. The column was eluted with a mixture of methanol and petroleum ether (1:9), giving a yield of ca. 6% of "adsorbate". The column was then further treated with hot methanol, and 0.2% more material was recovered. The main chemical investigation was made on the larger fraction removed by methanol and petroleum ether.

Experimental

General experimental methods

Alkali-refining. Peanut oil was treated at ca. 94C with a 25% excess (based on the free fatty acid content of the oil) of 4N aqueous caustic soda. The oil was then washed with water and dried in vacuo.

Saponification. The adsorbate (100 g) was refluxed for 1½ hr with a solution of potassium hydroxide (36 g) in aqueous methanol (800 ml; 1:4). Unsaponifiable matter was extracted with ether. Acidification, followed by ether extraction of the aqueous residue, gave the fatty acids.

Acid-catalysed esterification of fatty acids. The fatty acids were refluxed for 1–2 hr with a fourfold amount (v/v) of methanol containing 1% concd sulphuric acid or hydrochloric acid. The reaction product was diluted with water and the esters isolated from the aqueous layer by ether extraction.

Alkali-catalysed methanolysis. One part dry metha-

TABLE I
Analysis of Eluted and Adsorbed Peanut Oil

	Hydroxyl value	'vic.-Dioxy' content ^a	Lea figure	Unsaponifiable material	UV absorption coefficients maxima [E (1%, 1 cm)]
Alkali-refined peanut oil	2.4	0.43%	6.9	0.72%	E _{230 mμ} = 11 E _{275 mμ} = 0.7
Alkali-refined and alumina-treated peanut oil	1.1	0.18%	0	0.46%	No max. at 230 mμ E _{275 mμ} = 0.6
Alumina adsorbate	77.1	9.90%	10–15	3.8%	E _{231 mμ} = 104 E _{270 mμ} = 10

^a The term 'vic.-dioxy content' refers to the content of compounds of assumed average molecular weight 300 which are fissioned by periodic acid at room temperature. As this fission occurs not only with vic.-diols but also to some extent with vic.-dicarbonyl and vic.-carbonylhydroxy compounds, the term 'vic.-dioxy content' is not necessarily indicative of vic.-diol.

TABLE II
Chromatographic Separation of the Adsorbate on Silica Gel

Eluant	% Wt	Tentative identity based on IR spectra	UV absorption maxima (in ethanol)	Phosphatide ^a present	Sterol or sterol ester ^a present
4% ether/P.E.	16	Triglyceride (trace of OH)	E _{208 mμ} = 6 E _{280 mμ} = 5.5	No	Yes
8% ether/P.E.	66	Di- + hydroxylated triglyceride	E _{233 mμ} = 99	No	Yes
25% ether/P.E.			E _{273 mμ} = 6.0		
Ether	11	Monoglyceride + hydroxylated di- + triglycerides	E _{233 mμ} = 228 E _{271 mμ} = 79	No	Yes
Methanol	7	Highly hydroxylated material	E _{233 mμ} = 35 E _{270 mμ} = 25	Yes	No

^a Phosphatides and sterol/sterol esters were detected by tests based on reactions with methyl violet base and acetic anhydride/concd sulphuric acid respectively.

TABLE III
UV Absorption Maxima of the Adsorbate and the Methyl Esters of Its Fatty Acids

	E (1%, 1cm) 233 m μ	E (1%, 1cm) 259 m μ	E (1%, 1cm) 268-270 m μ	E (1%, 1cm) 279 m μ
Adsorbate	104	—	10	—
Fatty acids of the adsorbate	112	—	—	10
Methyl esters of adsorbate prepared by esterification of the fatty acids	47	112	149	116
Methyl esters of adsorbate prepared by alkali-catalysed methanolysis	100	—	6	—

nol containing sodium (0.5% based on weight of the adsorbate) was gradually added to 4 parts adsorbate at ca. 60C and the mixture refluxed for 1/2 hr. The reaction mixture was diluted with water and extracted with ether to give the methyl esters.

Lea value. Lea value is the peroxide value expressed in millimoles of oxygen-peroxide/kg of adsorbate. It was determined by adding KI to the adsorbate (in CHCl₃/AcOH) and titrating the liberated iodine with thiosulphate.

Preliminary analysis

Comparative analytical data (Table I) for alkali-refined peanut oil, alkali-refined and alumina-treated peanut oil, and the material retained by the alumina showed that hydroxylated material, unsaponifiable matter, and compounds containing conjugated diene and triene systems, were concentrated on the alumina. The small amount of hydroperoxide originally present in the alkali-refined oil was almost entirely destroyed.

To establish whether off-flavor precursors were concentrated in the two fractions eluted from the alumina column with methanol/petroleum ether and hot methanol, 1% solutions of each fraction in bland paraffin, and 1% solutions of each fraction in edible peanut oil, were prepared and stored at room temperature. Neither fraction caused the rate of deterioration of either oil to increase. Organoleptic assessments were carried out by a small panel of expert tasters. It

TABLE IV
Chromatography of the Methyl Esters of the Fatty Acids of the Adsorbate on a 6-Fold Amount of Silica Gel

Fraction	Eluant	% Wt	I. V.	Hydroxyl value	% 'vic.-Dioxy content'
1	Petroleum ether	48.2	62.1	0	0
2	2% ether/P.E.	36.3	129.5	2.0	0
3	Ether, chloroform and methanol	15.4	96.3	151.0	20.7
—	Unchromatographed methyl esters	—	97.0	21.4	4-5

appears, therefore, that the off-flavor precursors were chemically modified during the treatment on alumina.

It was decided to investigate further the larger fraction removed from the column with methanol and petroleum referred to as adsorbate.

Chromatographic separation of the adsorbate on silica gel

Chromatography (under nitrogen) of the adsorbate on a 30-fold amount of silica gel (100/200 mesh, containing 5% water) gave clear-cut separations. A typical separation is shown in Table II. Infrared spectra of the fractions indicated that, although the bulk of the adsorbate consisted of normal di- and triglycerides, considerable proportions of glycerides containing hydroxyl groups in the fatty chains were present. Furthermore, the ultraviolet adsorption was concentrated in the more polar, i.e., hydroxylated glyceride, fractions.

Storage tests of the individual fractions confirmed the absence of concentrates of off-flavor precursors.

Phosphatides and unsaponifiable material of the adsorbate

The phosphatides of the adsorbate were isolated by dialysis of a solution of the adsorbate in petroleum ether through a rubber membrane (2). The unsaponifiable material, isolated in the usual way, consisted of 73% β sitosterol and ca. 26% of a viscous oil; the latter was probably a concentrate of volatile aldehydes and had a pronounced bitter off-flavor. Neither the phosphatides nor the unsaponifiable material increased the rate of deterioration of edible peanut oil.

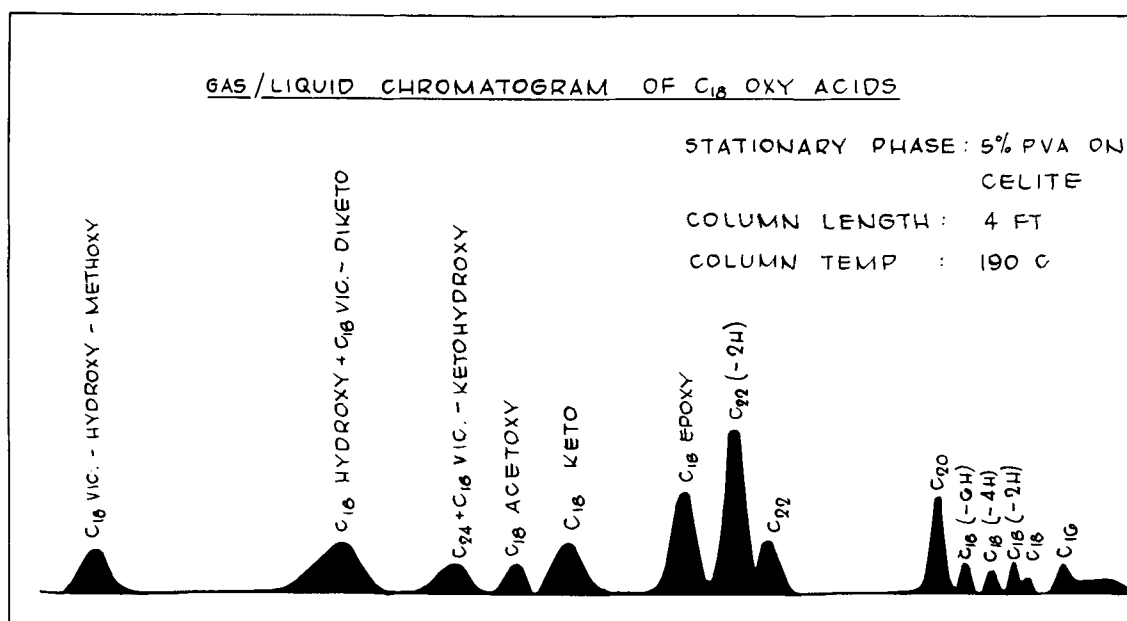


Fig. 1.

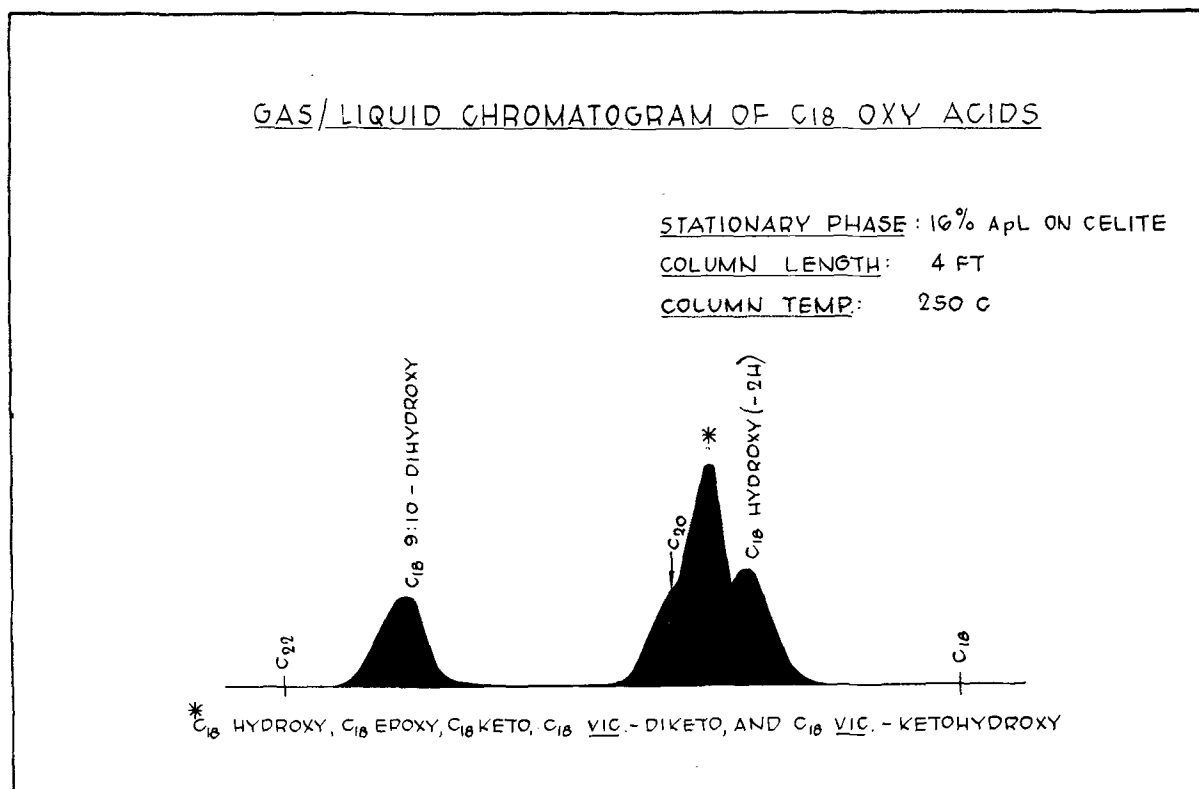


FIG. 2.

Fatty acids of the adsorbate

The fatty acids of the adsorbate were analysed as their methyl esters. The methyl esters were prepared a) by saponification of the adsorbate, removal of unsaponifiable material, followed by esterification of the fatty acids with methanol containing coned sulphuric acid as catalyst, or b) by alkali-catalysed methanolysis of the adsorbate. The ultra-violet absorption characteristics of the methyl esters were found to depend on the method of preparation (Table III).

Saponification or alkali-catalysed methanolysis of the adsorbate, to give fatty acids and methyl esters respectively, did not affect the ultra-violet absorption of the fatty material significantly. However, acid-catalysed esterification of the fatty acids gave a triple peak at 259-279 $m\mu$, while the extinction coefficient at 233 $m\mu$ was reduced.

Methyl esters prepared by acid-catalysed esterification of the fatty acids of the adsorbate were employed for chromatographic analyses.

Column chromatography on silica gel did not give simple fractions, but resulted in a concentrate of oxygenated fatty acid methyl esters as shown in Table IV.

The total methyl esters and the above chromatographic fractions were further analysed by GLC on two columns: a.) 4-ft column packed with 5% polyvinyl acetate (PVA) on celite at 180-200C; b.) 4-ft column packed with 16% Apiezon L (Ap L) on celite at 180-250C. Both columns are satisfactory for chromatography of C₈-C₂₄ unsubstituted fatty acid methyl esters but column a is more suitable for the separation of simple, oxygenated fatty acid methyl esters.

The separations of model mixtures achieved with columns a and b are shown in Figures 1 and 2, respectively. On PVA/celite, C₁₈ keto, C₁₈ hydroxy and C₁₈ epoxy acids gave separate peaks. Separation

of individual saturated and unsaturated C₁₈ hydroxy-acids did not occur; 9-hydroxy, 10-hydroxy, 12-hydroxy, 2-hydroxy-octadecanoic acid, 9-hydroxyoctadec-12-enoic and 12-hydroxyoctadec-9-enoic acid were all eluted at the same position. 9:10-Diketo- and 9/10-ketohydroxyoctadecanoic acid were eluted at the C₁₈ hydroxy and C₂₄ positions respectively but could be distinguished by reducing or acetylating the methyl esters before chromatography. Dihydroxyoctadecanoic acid was not eluted from the PVA/celite system. On Ap L/celite, a mixture of C₁₈ hydroxy (saturated), C₁₈ epoxy, C₁₈ keto, C₁₈ vic.-diketo, and C₁₈ vic.-keto hydroxy acids gave a single peak near the C₂₀ position. Unsaturated C₁₈ hydroxy acids were eluted just before the corresponding saturated acids, but the difference in elution times was too small for reliable identification. 9:10-dihydroxyoctadecanoic acid gave a peak near the C₂₂ position; the *threo*- and *erythro*-isomers could not be separated. Ap L/celite thus appears not to be a good medium for separation of oxygenated acids.

The methyl esters of the adsorbate were shown to correspond to a complex pattern of unsubstituted and oxidized fatty acids; some of the components could only be detected when concentrated sufficiently in a particular column chromatographic fraction (cf. Table IV). Typical GL chromatograms of the total methyl esters and a concentrate of oxygenated methyl esters (i.e. fraction 3 in Table IV) are shown in Figures 3 and 4, respectively. The overall analysis, as obtained by GLC of the total methyl esters and individual fractions, enabled the identification of the components set out in Table V. Some of the unidentified peaks in Figures 3 and 4 probably represent partially polymerized or highly oxidized fatty acids.

GLC of the methyl esters of aldehydoacids, investigated in connection with aldehydoglycerides found in the adsorbate (below), on either of the two

TABLE V

Fatty Acids of the Adsorbate Identified by GLC on PVA/celite and Ap L/celite

Fatty acid	%
C ₈₋₁₄	Traces
C ₁₆	ca. 15
C ₁₈	
C ₁₈ (-2H) }	ca. 60
C ₁₈ (-4H) }	
C ₁₈ (-6H) }	
C ₂₀	ca. 1.5
C ₂₂	ca. 3.0
C ₂₂ (-2H)	ca. 1.0
C ₂₄	ca. 2.0
C ₁₈ epoxy	0.5-1.0
C ₁₈ hydroxy	ca. 3.0
C ₁₈ keto	Traces
<i>Threo</i> -9:10-dihydroxyoctadecanoic acid (confirmed by crystallization of the methyl esters of the adsorbate)	1.0-2.0
Unidentified	ca. 12
	ca. 100%

stationary phases gave inconclusive results; oxidation or polymerization probably occurred on the columns.

Aldehydoglycerides

Carbonyls were isolated almost quantitatively from the adsorbate by passage of a solution in carbonyl-free n-hexane through a column of 2:4-dinitrophenylhydrazine hydrochloride suspended on a celite support (3). The carbonyls from the methyl esters of

the fatty acids of the adsorbate were isolated similarly. The 2:4-dinitrophenylhydrazones were chromatographed on paper, using synthetic reference compounds, and the nature of the non-volatile carbonyls originally present in the adsorbate determined from the two results.

The 2:4-dinitrophenylhydrazones isolated from the adsorbate were concentrated by chromatography on deactivated alumina (grade H, ex P. Spence Ltd. 5% of 10% aqueous acetic acid) 60% of unreacted fatty material being removed. Although the hydrazone fractions were eluted as relatively sharp bands, they were contaminated with non-carbonylic fatty material. The weights and extinction coefficients of the hydrazone fractions are given in Table VI. The 2:4-dinitrophenylhydrazones were further characterized by chromatography on Whatman No. 1 paper impregnated with a 15% solution of paraffin oil in petrol, using dioxane-water (3:1) saturated with paraffin oil as eluant.

The presence of aldehydoglycerides in the adsorbate was confirmed by analysing the 2:4-dinitrophenylhydrazone fractions derived from the methyl esters of the adsorbate fatty acids. Chromatography on unimpregnated Whatman paper, using iso-octane saturated with methanol as mobile phase, showed one of the fractions to be methyl aldehydo-9-nonanoate 2:4-

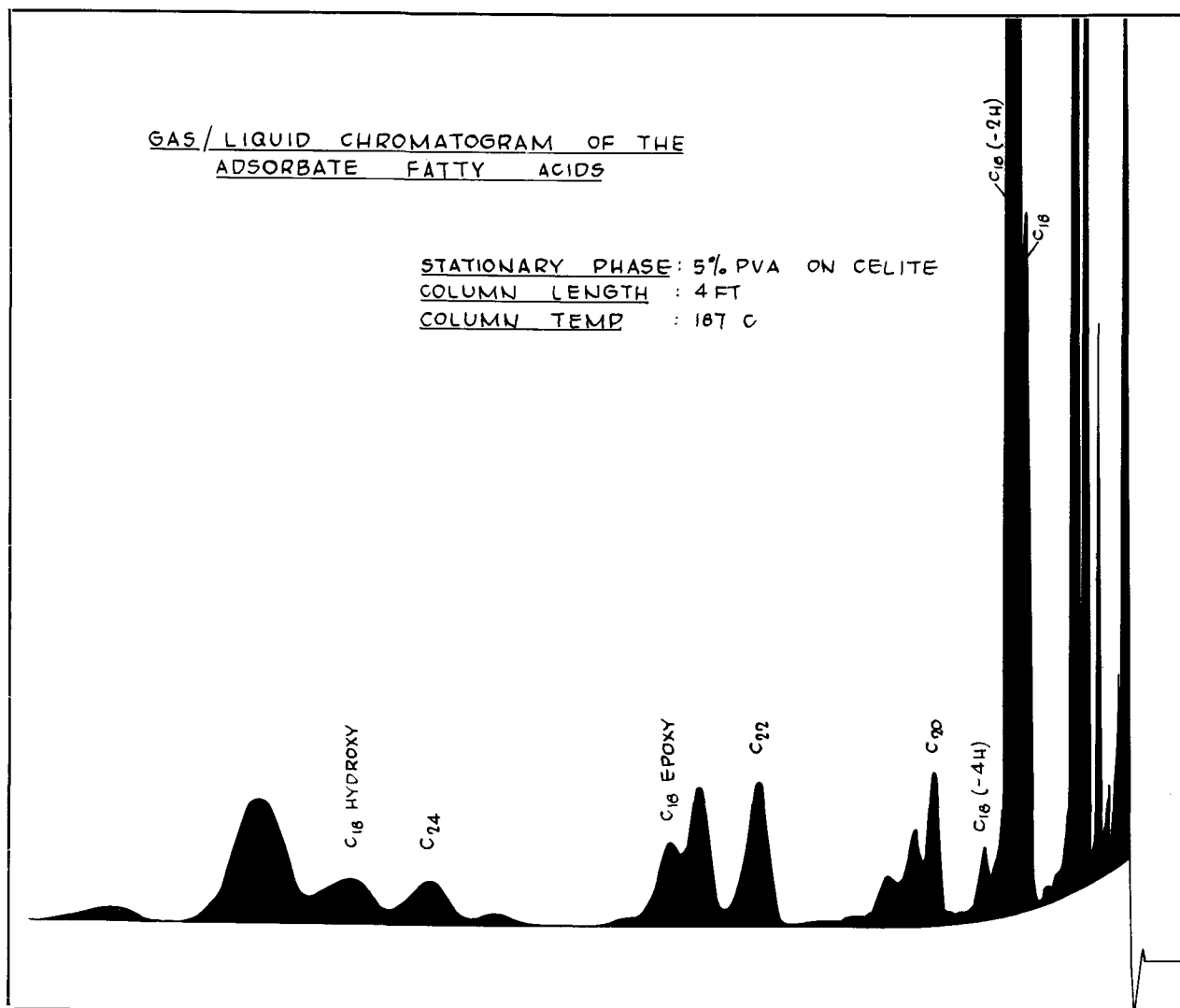


FIG. 3.

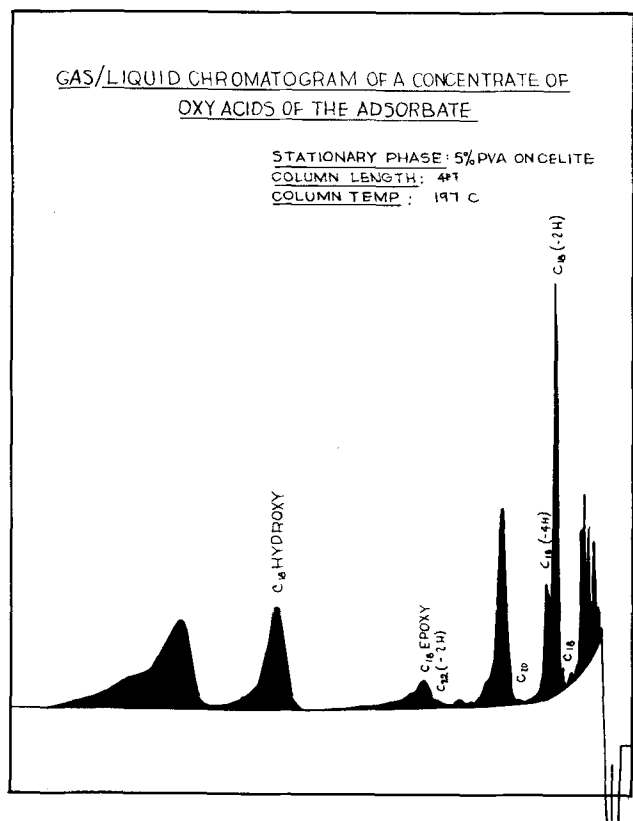


FIG. 4.

dinitrophenylhydrazone by comparison with synthetic material (Table VII). The other fractions probably represent the 2:4-dinitrophenylhydrazones of the methyl esters of C_8 to C_{10} acids containing an aldehyde group. Methyl ketostearate could not be detected by chromatography on untreated or impregnated paper.

Discussion

Storage tests showed that off-flavor precursors are not concentrated in the adsorbate. This fact was substantiated by testing the individual chromatographic fractions, unsaponifiable material, and phosphatides of the adsorbate. Off-flavor precursors appear to be largely modified on activated alumina. Alumina treatment may owe its effectiveness in producing good quality oils to removal of off-flavor precursors by adsorption; to deactivation of them on the column; to suppression of precursor and oxidant formation; and to the mildness of the treatment.

Preliminary analyses of the adsorbate (Table I) showed that activated alumina removes, as expected, hydroxylated material and unsaponifiable matter from a solution of peanut oil in petroleum ether. Furthermore, chromatographic separation of the adsorbate on silica gel (Table II) established that the hydroxylated material consists not only of partial glycerides, but contains a considerable proportion of glycerides of hydroxy fatty acids.

Fatty acids of the adsorbate

Chromatography of the fatty methyl esters, prepared by acid-catalysed esterification of fatty acids on silica gel, did not fractionate the esters into individual compounds but gave a concentrated mixture of oxygenated esters. GLC of the methyl esters led to the identification of C_{18} epoxy (0.5–0.1%), C_{18} hydroxy-

TABLE VI
Isolation of Aldehydoglyceride-2:4-dinitrophenylhydrazones

Column chromatography on deactivated alumina			Paper chromatography		
Fraction ^a	% Wt	E (1%, 1cm) absorption maximum (in $CHCl_3$)	Rf-value	Color with alc. KOH solution ^b	Suggested identity of parent compound
1	10	E (1%, 1cm) at 373 $m\mu$ = 4.0	0.095	No	Triglyceride containing saturated and/or α , β -unsaturated aldehyde group.
			0.111	Yes	
2	18	E (1%, 1cm) at 383 $m\mu$ = 14.3	0.233	Yes	Triglyceride containing α , β - (and α , β , γ , δ -?) unsaturated aldehyde group. Partial glyceride containing α , β -unsaturated aldehyde group.
			0.136	Yes	
3	2	E (1%, 1cm) at 376 $m\mu$ = 30.0	0.5–0.7 (traces)	Yes	Partial glyceride containing α , β -unsaturated aldehyde group. C_8 to C_{10} 2,4-dienals and C_8 to C_9 2-enals
			0.096	No	
Reference compound (7)			0.096	No	DNPH of 1-(aldehydo-9'-nonanoyl)-2:3-dipalmitin

^a 60% of non-carboxylic material was removed during the separation.
^b Indicative of presence of dienal.

(ca. 3%), 9:10-dihydroxyoctadecanoic (1.0–2.0%), and possibly traces of C_{18} keto acid in addition to the fatty acids usually found in peanut oil (Table V). The C_{18} monohydroxy-acids are probably a mixture of saturated and unsaturated hydroxy acids; mixtures of synthetic saturated and monounsaturated C_{18} hydroxy-acids could not be separated on the stationary phases employed. Some of the unidentified components (ca. 12%) probably represent partially polymerised or highly oxidised fatty acids. Since the *vic*-dioxy content, determined by periodate titration, of the adsorbate fatty acid methyl esters is 4–5% (based on an average molecular weight of 300; see Table IV), and only 1–2% of *vic*-dihydroxystearic acid could be detected (*vic*-ketohydroxy and *vic*-diketo acid were not present), it appears that some of the unidentified components react with periodic acid.

The symmetry of the chromatogram peaks in Figures 1 and 2 suggests that decomposition on the stationary phase of the simple synthetic reference compounds investigated is not extensive. It may be noted that Morris et al. (4) have shown that hydroxy

TABLE VII
2:4-Dinitrophenylhydrazones Isolated from the Methyl Esters of the Fatty Acids of the Adsorbate

Fraction	Absorption maximum (in $CHCl_3$)	Rf-value	Identity
1	370 $m\mu$	ca. 0.750	Probably the 2:4-dinitrophenyl hydrazone of the methyl ester of a C_{10-12} acid containing a 2-enal group.
2	366 $m\mu$	ca. 0.660	Probably the 2:4-dinitrophenyl hydrazone of the methyl ester of a ca. C_{10} aldehyde acid.
3	359 $m\mu$	0.507	Methyl aldehydo-9-mononate 2:4-dinitrophenylhydrazone.
4	369 $m\mu$	0.449	Probably the 2:4-dinitrophenyl hydrazone of the methyl ester of a C_8 or C_9 acid containing a 2-enal group.
—	—	0.9–0.95	Methyl ketostearate-2:4-dinitrophenylhydrazone (Reference compound).

compounds not activated by adjacent unsaturation are stable during GLC analysis whereas α -hydroxymonoenes and α -hydroxydienes, e.g. methyl dimorphecolate, are dehydrated to give conjugated dienes and trienes respectively.

The adsorbate appears to contain hydroxy acids with a conjugated diene system adjacent to the hydroxyl group which are not detected as such by GLC on Ap L/celite.

A considerable increase in the conjugated triene adsorption (ca. 270 $m\mu$) at the expense of the conjugated diene adsorption (ca. 230 $m\mu$) results when esterifying the fatty acids of the adsorbate with acidic methanol (Table III). This increase could be due to acid-catalysed dehydration of a conjugated hydroxydiene (4,5,6), since alkali-catalysed methanolysis of the adsorbate does not affect the ultraviolet adsorption significantly.

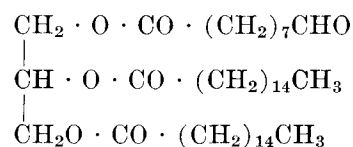
The triple peak at 270 $m\mu$ could be due entirely to a conjugated triene system or to a mixture of conjugated triene and conjugated dienone. Lithium aluminium hydride reduction of methyl esters, prepared by acid-catalysed esterification of the fatty acids of the adsorbate, decreased the extinction coefficient at 268 $m\mu$ from 149–129, while the extinction coefficient at 233 $m\mu$ was increased from 47–55. This behaviour indicates that the triple peak of the unreduced methyl esters at 259–279 $m\mu$ corresponds to ca. 90% of conjugated triene, while the remaining 10% of material probably contains a 2-4 dienal system, which, on reduction, will give a conjugated hydroxydiene absorbing at ca. 233 $m\mu$.

Retention of glycerides containing hydroxydiene fatty acids (probably produced by breakdown of hydroperoxides on alumina or during prior refining) on alumina is also indicated by the simultaneously higher hydroxyl value and diene absorption at 231 $m\mu$ of the adsorbate as compared to untreated, neutralised peanut oil (Table I). From the extinction coefficient $E(1\%, 1\text{ cm})$ of methyl dimorphecolate (i.e. methyl-9-hydroxy-*trans,trans*-10,12-octadecadienoate, a known ester containing an hydroxyl group adjacent to a conjugated diene) at 231 $m\mu$ (5), and the observed decrease in extinction coefficient at ca. 230 $m\mu$ on esterifying the fatty acids of the adsorbate with acidic methanol (Table III), the adsorbate fatty acids can be estimated to contain ca. 7% of hydroxy acids with a conjugated diene system adjacent to the hydroxyl group. Since GLC indicates ca. 3% of C_{18} monohydroxy acids (see Table V), the total content of monohydroxy acids in the adsorbate appears to be ca. 10% (i.e. 3% + 7%), corresponding to more than 1% of the original peanut oil.

Bleaching of the oil with active earth tends to dehydrate hydroxydienes to more oxidizable trienes. Such dehydration does not occur with alumina treatment, and may be one of the factors accounting for the superiority of alumina treatment over earth bleaching.

Aldehydoglycerides

Examination of the carbonyl compounds in the adsorbate led to the identification of aldehydoglycerides, in addition to traces of volatile 2-enals and 2,4-dienals, as paper chromatographic spots with low R_f values (Table VI). The R_f value on paper of the 2:4-dinitrophenylhydrazone of one of the component aldehydoglycerides was identical with that of a synthetic sample of 1-(aldehydo-9'-nonanoyl)-2:3-dipalmitin-2:4-dinitrophenylhydrazone:



In conjunction with infrared and ultraviolet absorption data, the R_f values of the spots suggest that the adsorbate contains triglycerides and partial glycerides having saturated, α , β -unsaturated, and traces of α , β , γ , δ -diunsaturated aldehyde groups. Traces of 2:4-dinitrophenylhydrazones of C_8 to C_{10} 2:4-dienals, and C_8 to C_9 2-enals were also detected on paper. The suggested identities of the paper-chromatographic spots are given in Table VI.

Measurement of the ultraviolet absorption of the dinitrophenylhydrazones indicates that the adsorbate contains about 2% of aldehydoglycerides, the bulk of which has at least one double bond conjugated with the carbonyl group. The isolation of aldehydoglycerides from the oil is timely since there has been much speculation on the nature and function of non-volatile carbonyl compounds of vegetable oils. Lea and Swoboda (7) have shown the presence of non-volatile carbonyls in oils and several workers (8) have expressed the belief that non-volatile carbonyls of high molecular weight are precursors of volatile odorous substances. Although there is no doubt that non-volatile carbonyl compounds appear in oils, it is clear that the carbonyl determinations used by many workers have estimated, not only carbonyls, but also hydroperoxide; published quantitative measurements are therefore frequently misleading.

Non-volatile carbonyl compounds in oils are most likely to be formed by oxidation of unsaturated glycerides. The main possibilities are the formation of oxidized glycerides of similar chain length, such as keto-unsaturated compounds formed by oxidation near the double bond or, alternatively, aldehydoglycerides formed by oxidative scission (9). Present work suggests that for peanut oil the latter mechanism predominates.

It is possible that on alumina the relatively small amounts of hydroperoxides in peanut oil decompose into conjugated hydroxydienes (above), whereas aldehydoglycerides are formed by breakdown of hydroperoxides during refining before treatment with alumina. A synthetic sample of 1-(aldehydo-9'-nonanoyl)-2:3-dipalmitin is strongly adsorbed from petrol solution on activated alumina. It follows, therefore, that alumina treatment of oils may have an advantage over a bleaching process with a relatively small amount of active earth by virtue of more effective removal of aldehydoglycerides.

A study of the properties of synthetic aldehydoglycerides and related compounds is in progress and will form the basis of a future publication.

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[Received October 19, 1961—Accepted May 13, 1963]