as compared with a value of 95% obtained for another protein (No. 5, Table I), previously prepared from a different lot of lye-dipped peanuts. This variation may be due to differences in skin pigment content of peanuts from different sources and treatments.

Summary

A method for estimating the skin content of peanut meals and relative skin pigment content of peanut proteins is described. The method is based on the fact that the pigments consist predominantly of a catechol tannin and related compounds which give a red product with characteristic absorption when heated with alcoholic hydrochloric acid.

Any residue of red skins imparts color to peanut meals and protein products derived from them. Since this color is objectionable to the use of these products for industrial purposes and may be an important consideration in the future use of extracted peanut meal in foods, the method was applied to meals containing known amounts of skins and to proteins of known processing history. The results obtained indicate that the method may be used to estimate the degree of skin removal in the preparation of peanut meals and also to evaluate proteins for skin pigment content.

Acknowledgment

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Volatile Cleavage Products of Autoxidized Soybean Oil[1]

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THE isolation and identification of volatile substances which, in trace amounts, contribute to the odors and flavors of food products constitute a most difficult field of research. There is no physical or chemical test which can rival the human sense of smell or taste. Research in this field must necessarily involve a many-fold concentration of volatile flavor principles and use of highly developed micro-chemical techniques.

A pioneering step in the study of the flavor problem of soybean oil and of soybean shortening was taken by Daubert and co-workers (9, 12, 14), who collected the volatile materials from as many as 275 successive "reversions" and deodorizations. In this condensate they were able to identify acetaldehyde, α-heptenal, and 2,4-decadienal from soybean oil and maleic dialdehyde, di-n-propyl ketone, and α-heptenal from soybean oil shortenings as their respective 2,4-dinitrophenylhydrazones (DNPH's). Since Daubert's "reversion" procedure for the soybean salad oil consisted of heating the oil to 200°C., it appeared that isolation and identification of odor constituents formed at low temperature would be of considerable practical interest with regard to the storage flavor of soybean salad oil. A further innovation in the work to be described consisted of chromatographic fractionation of the odor constituents upon silicic acid into what has been characterized by experienced taste panel members as "reverted" and "rancid" components prior to formation of the 2,4-dinitrophenylhydrazone derivatives. After another chromatographic separation step the colored derivatives, and consequently the original aldehydes, were identified by melting points, ultimate analyses, and R_f values.

[1]Presented at the October 1951 meeting of the American Oil Chemists' Society, Chicago, Ill.

[2]One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

Materials and Methods

The pentane-hexane used for ultraviolet spectroscopy was prepared by distillation and by passage through silicic acid according to the method of Graff (7). For chromatographic separation of DNPH's purification of the pentane-hexane was by distillation.

Chromatographic grade silicic acid (100-mesh size), procured from the Mallinckrodt Company[3] (Lot 2847, Control Van-1), was mixed with Johns-Manville Super-cel[3] (code A66050) and served as adsorbent.

The absolute ethanol was purified by refluxing over zinc and potassium hydroxide and was distilled through a fractionating column.

Diethyl ether (Baker's (A.C.S.) was used without further treatment.

The stock solution of *m*-phenylene diamine hydrochloride used for the detection of α-β unsaturated carbonyls was prepared by dissolving 1.0 g. of the reagent in 250 ml. of water (16).

Five-milliliter fractions from the chromatographic column were caught in a collector manufactured by the Technicon Chromatography Corporation.[3]

2,4-Dinitrophenylhydrazones were prepared by dissolving the samples in 100 to 150 ml. of aldehyde-free ethanol in the presence of 1 ml. of concentrated hydrochloric acid and 1 to 2 g. of 2,4-dinitrophenyl-

[3]The mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

hydrazine. The mixture was heated to boiling for 1 minute, cooled, and extracted with diethyl ether. The ether extract was washed free of acid, and the ether evaporated under reduced pressure.

The odor condensates were fractionated into reverted and rancid components by adsorption analysis as detailed below:

Adsorbent—silicic acid + super-cel (1 + 1) with 5.0% florophors (13)

Column—1.9 cm. × 20 cm. quartz

Developer—5% purified ethanol in purified pentane-hexane

Pore volume of column—59 ml.

Rate of percolation—2 drops/5 sec.

Pressure—(oxygen-free nitrogen) 0.5 lbs./in.^{2}

Volume per fraction—5.0 ml.

The 2,4-dinitrophenylhydrazones were chromatographed according to the following procedure:

Adsorbent—silicic acid + super-cel (2 + 1), *ca* 240 gm. per column

Column—5.3 cm. × 30 cm. packed to 25 cm. height

Solvent for introduction—150 ml. benzene

Wash—100 ml. pentane-hexane

Developer—3% diethyl ether in distilled pentane-hexane

Rate of percolation—1 drop/sec.

In order to concentrate and isolate the volatile odor constituents of reverted soybean oil, a 5,600-ml. batch of deodorized soybean oil (5,062 g.) containing 5 mg. of $FeCl_3$ and 5 mg. of Cu_2Cl_2 was heated to 60° for 3 days and thereafter kept at 37°C. A stream of oxygen was continuously bubbled through the oil. The issuing gases were bubbled through 10-ml. of purified pentane-hexane contained in a glass trap immersed in a solid CO_2-ethanol bath.

Results

Preliminary tests were made of the volatile odor condensate from the autoxidized soybean oil to determine whether the odor responsible for flavor reversion was aldehyde in nature. Neutralization of volatiles to phenolphthalein in pentane-hexane had no effect in removing the odor. However the reversion odor was removed by the addition of dilute sodium bisulfite solution and by use of the hydroxylamine reagent.

After 12 days of autoxidation and collection of volatiles as described above, the contents of the trap were fractionated into painty and rancid components by the adsorption analysis. The autoxidation and collection was continued three more days for the second run.

The progress of the descending fluorescent band was followed by illumination with ultra-violet light at intervals. The adsorbed solutes appeared as a shadow in the fluorescent column and probably were aldehydes, as shown later. After the percolate had been collected in 48 test tubes of the fraction collector, the position, quality, and intensity of odors were assayed organoleptically by at least three experienced members of the taste panel. These data along with optical densities at 265 mμ are given in Figure 1. It appears that the elution of two ultraviolet-light-absorbing components is correlated with the elution of odors of

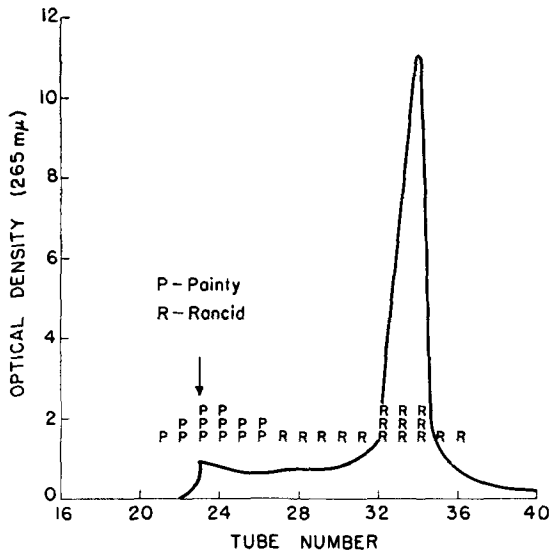


FIG. 1. Adsorption analysis of volatiles collected from the autoxidation of soybean oil. Optical densities and organoleptic evaluations are plotted against fraction number. The arrow indicates the point of emergence of fluorescence-quenching solutes.

different quality. The first component, fractions 21 through 26, was characterized as painty, and the second, fractions 27 through 36, as rancid. The elution of the fluorescence-quenching solutes was found to coincide with the emergence of the painty fraction. The vertical arrow in Figure 1 indicates the point of elution.

Fractions from 23 through 38 were tested for α-β unsaturation by adding 0.5 ml. of *m*-phenylene diamine stock reagent (3) to a 0.5 ml. aliquot of the fraction diluted with 1 ml. of purified absolute ethanol. Fractions 23, 24, and 25 gave a strong yellow coloration for the painty component, and fractions 34 and 35 likewise gave a strong yellow coloration in contrast to the blank test which was violet. The coloration was recorded one minute after the addition of reagents.

Fractions 23 through 26 which were described as painty were combined and converted to the 2,4-dinitrophenylhydrazones.

These were then chromatographed as described in the "methods" section. The chromatogram was permitted to develop by percolation until 5,075 ml. of eluate was collected. By this technique the following bands were observed:

Bands	Color	Position	Weight
A	Red	5 cm. to 5.6 cm.	0.2181 g.
B	Diffuse	5.7 cm. to 10.9 cm.	0.0187 g.
C	Red	11cm. to 11.1 cm.	0.0084 g.
D	Yellow-orange	11.3 cm. to 16.5 cm.	0.1759 g.
D_2	Diffuse	16.5 cm. to 18 cm.	0.0265 g.
E		Eluate	?

The column was dried free of solvent with the aid of vacuum, the bands were cut out and eluted with diethyl ether, and the ether was evaporated under reduced pressure. Band D was rechromatographed for further purification. The main band of D yielded 151 mg. of DNPH. The derivative was recrystallized three times from 80% ethanol, yielding yellow plates which melted at 164°-165°C. [m.p. 168.5°C. for acetaldehyde DNPH; Bryant, J.A.C.S. *60*, 2815 (1938)]; *Anal. Calcd.* for $C_8H_8N_4O_4$: C, 42.86; H, 3.60; N, 24.99. Found: C, 43.0; H, 3.57; N, 25.00. Since the other

bands were investigated more completely in a subsequent experiment, their discussion is omitted here.

A second collection of soybean oil volatiles, accumulated in the following three days was fractionated on silica as described above. Fractions collected in 5.0 ml. volume were again evaluated organoleptically; fractions 17 through 22 were described as painty while those from 23 through 29 were characterized as rancid. Spectrophotometric curves of fractions 19 and 23 were selected for presentation as these represented the concentration peaks of the painty and rancid components, respectively. In Figure 2 the curve for fractions 19 and 23 is given and shows that fractionation did take place on the silicic gel with respect to the two ultra-violet absorbing components.

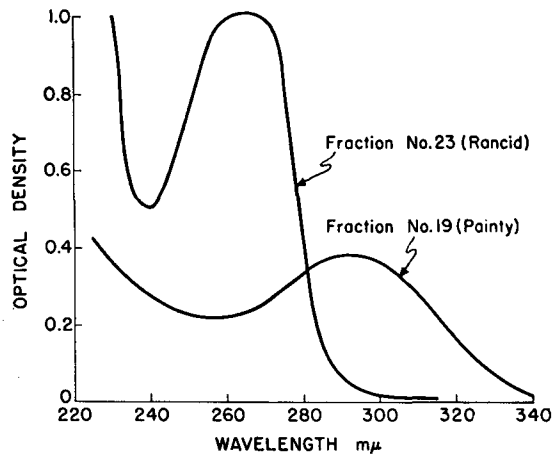


FIG. 2. Spectrophotometric curves of volatiles of soybean oil fractionated on silicic acid. Sample 19 is from the "painty" fraction (diluted 5 times with pentane-hexane); sample 23 is from the rancid fraction (diluted 250 times with pentane-hexane).

Fractions 17 through 22, representative of the painty components, were collectively converted to the 2,4-dinitrophenylhydrazones. Likewise the rancid fractions from 23 through 27 were collectively converted to the 2,4-dinitrophenylhydrazones.

The composite mixture (.4248 g.) as DNPH from the painty components was placed upon a chromatographic column, and the chromatogram was permitted to develop by percolation until 2,080 ml. of eluate were collected. The following bands were resolved:

Bands	Color	Position	Weight
Pa	Red	3.8 cm. to 4.1 cm.	
Pb	Yellow	6 cm. to 8 cm.	.1199 g.
Pc	Yellow	9.4 cm. to 12 cm.	
P_B	Yellow-orange	14.5 cm. to 24 cm.	.2891 g.

The column was dried free of solvent by aid of vacuum, the bands cut out and eluted with ether, and the ether removed under reduced pressure. Since the column was obviously overloaded, fractions Pa, Pb, and Pc were combined to be rechromatographed.

Band P_B (0.2891 g.) was rechromatographed in a similar manner. No further fractionation resulted, though diffuse areas appeared at the top and bottom of the main band. The main section of the principal band was cut out, and the DNPH (123.6 mg.) obtained in the usual manner. After two recrystallizations from 80% ethanol the melting point was 93.5°-95°C. [m.p. 104°C. for hexanal DNPH; Allen, J.A.C.S. *52*, 2957 (1930)]; *Anal. Calcd.* for $C_{12}H_{16}N_4O_4$: C, 51.40; H, 5.63; N, 20.1. Found: C, 52.2; H, 5.78; N, 20.01.

The composite Pa, Pb, Pc was rechromatographed in the usual manner, yielding the following chromatogram when 2,926 ml. of eluate was collected:

Band	Color	Position	Weight
$P_A{}^1$	Red	4.2 cm. to 5 cm.	12 mg.
$P_B{}^1$	Yellow	9 cm. to 11.2 cm.	93.3 mg.
$P_C{}^1$	Yellow	13.2 cm. to 15.6 cm.	18.4 mg.
$P_D{}^1$	Red	17.5 cm. to 20.2 cm.	5.8 mg.
$P_E{}^1$	Diffuse	28 cm.—	6.2 mg.

Fraction $P_B{}^1$ was chromatographed once more, using a 4.6 cm. x 27 cm. column. The resulting yellow plates melted at 157°-158°C. [m.p. 157°C. and 168°C. for acetaldehyde DNPH; Bryant, J.A.C.S. *60*, 2815 (1938)]; *Anal. Calcd.* for $C_8H_8N_4O_4$: C, 42.86; H, 3.60; N, 24.99. Found: C, 43.0; H, 3.87; N, 25.55.

As the amount of $P_C{}^1$ (18.4 mg.) made further purification by column method not feasible, it was recrystallized twice from 80% ethanol. After this treatment it melted at 150°-152°C. [m.p. 155°C. for propionaldehyde DNPH; Allen, J.A.C.S. *52*, 2957 (1930)]; *Anal. Calcd.* for $C_9H_{10}N_4O_4$: C, 45.38; H, 4.23; N, 23.52. Found: C, 45.7; H, 4.36; N, 23.9.

The 2,4-dinitrophenylhydrazones of the rancid component (0.4367 g.) were then chromatographed. The chromatogram was developed by gravity percolation until 3,270 ml. of eluate were collected, yielding the following zones:

Bands	Color	Position	Weight
R_A	Red	4.3 cm. to 5.5 cm.	196.6 mg.
R_B	Yellow	9.2 cm. to 11 cm.	81.5 mg.
R_C	Yellow-orange	13.5 cm. to 16.5 cm.	67.5 mg.
R_D	Red-orange	19 cm. to 25.5 cm.	82.8 mg.
R_E	Diffuse	25.5 cm.—	7.0 mg.

All bands were recovered as mentioned before. Band R_B was rechromatographed, the DNPH purified, isolated, and recrystallized three times from 80% ethanol, m.p. 165°-166°C.; *Anal. Calcd.* for $C_8H_8N_4O_4$: C, 42.86; H, 3.60; N, 24.99. Found: C, 43.3; H, 3.84; N, 25.2.

The R_C band was purified further by adsorption and isolated (61.5 mg.). Crystallization from 80% ethanol gave a product of m.p. 141°-148°C. Further crystallization failed to improve its purity appreciably. *Anal. Calcd.* for $C_9H_{10}N_4O_4$: C, 45.38; H, 4.23; N, 23.52. Found: C. 46.4; H, 4.43; N, 23.2. *Calcd.* for $C_{10}H_{10}N_4O_4$: C, 47.95; H, 4.03; N, 22.81.

The absorption spectra in purified absolute ethanol of crystals (R_C) and of propionaldehyde and of crotonaldehyde DNPH's are shown in Figure 3. Saturated aldehyde DNPH's, such as those of propionaldehyde and butyraldehyde (not shown), possess a maximum at 356 mμ and a minimum at 292.5 mμ while α-unsaturated aldehyde DNPH's, such as α-pentenal DNPH and crotonaldehyde DNPH, show maxima at 375 mμ and minima at 313 mμ. It is interesting to note that R_C has a maximum at 363 mμ and a minimum at 297 mμ. A second point of interest is the appearance of the second "shoulder" in the ultra-violet region of the absorption spectrum, at 280-290 mμ for the known crotonaldehyde DNPH, and at 270-280 mμ for R_C. As this second inflection

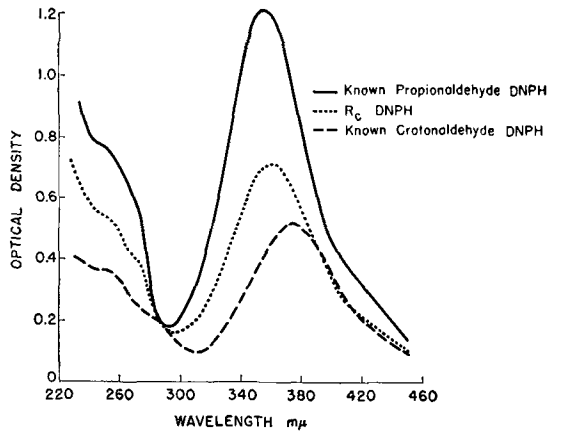


FIG. 3. Spectrophotometric curves for DNPH's of authentic crotonaldehyde and propionaldehyde, and a band (R_C) believed to be a mixture of the two which was isolated chromatographically from the rancid components.

is not present in the absorption spectrum for propionaldehyde DNPH, a conclusion might be drawn that R_C is a mixture of crotonaldehyde DNPH and propionaldehyde DNPH.

During the course of chromatographic separations of the 2,4-dinitrophenylhydrazones it was observed that rate of movement of bands could be related to the structure of the compound. Data were subsequently collected on rate of movement of known compounds and isolated aldehydes and are summarized in Table I.

TABLE I

R_F Values of 2,4-Dinitrophenylhydrazones of Aldehydes

Known preparations	R_F*
1. Formaldehyde	.0254
2. Acetaldehyde	.0263
3. Crotonaldehyde	.0551
4. Propionaldehyde	.0574
5. α-Pentenal	.0739
6. Butyraldehyde	.0868
7. Valeraldehyde	.1056
8. α-Heptenal	.1277
9. Hexanal	.1376
10. Heptanal	.1380
11. Octanal	.1611
Compounds derived from Soybean Oil	
1. R_B	.0234 (acetaldehyde DNPH)
2. R_C	.0532 (propionaldehyde DNPH) (crotonaldehyde DNPH)
3. R_D	.0854 (α-pentenal DNPH)
4. P_B[1]	.0357 (acetaldehyde DNPH)
5. P_C[1]	.0578 (propionaldehyde DNPH)
6. P_D[1]	.0830 (?)
7. P_E[1]	.1288 (hexanal DNPH)

* $\frac{\text{cm. traversed by solute.}}{\text{cm. traversed by solvent}}$

While "R_f" values have not been used previously to describe adsorption characteristics because of theoretical objections, they have nonetheless served in this work to give practical clues for qualitative identification. R_f is defined as a ratio of "centimeters traversed by solute" and "centimeters traversed by the developing solvent." Although there are some discrepancies of "R_f" values of known aldehydes and those identified by melting points and elementary analyses, they are on the whole in fairly good agreement. For example, the "R_f" value of known acetaldehyde DNPH is 0.0263 while that of R_B, which is acetaldehyde DNPH by ultimate analysis and melting point, is 0.0234. Known preparations of propionaldehyde DNPH (R_f =.0574) and crotonaldehyde DNPH (R_f=.0551) cannot be separated effectively as their respective rates of movement on silica are very nearly identical. This evidence supports the indications presented above, above, based on absorption spectrum, melting point range, and ultimate analyses, that the irresolvable fraction, R_C, is a mixture of crotonaldehyde and propionaldehyde DNPH's.

The red-orange band R_D was chromatographed again, isolated, and recrystallized twice from 80% ethanol. The deep-red needles melted at 149°-153°C. Yield 42.2 mg. ultimate analysis gave: C, 50.8; H, 5.01; N, 21.6.

Since this analysis was indicative of the 2,4-dinitrophenylhydrazone of a 5-carbon compound and its deep-red color indicative of an α,β-unsaturation, α-pentenal was prepared according to the method used by Daubert (8) for α-heptenal. Ethyl hydrogen malonate (121 g.) was condensed with 36 ml. of propionaldehyde in 300 ml. of water-free pyridine with 1 ml. of piperidine as catalyst (6). After refluxing on a steam bath for 6 hours, the mixture was extracted with diethyl ether and washed with 5% HCl in water. The ether was removed under reduced pressure, and the ethyl 2-pentenoate was distilled *in vacuo* under nitrogen: yield 51 g., b.p. 38°C./10 mm. Ethyl 2-pentenoate (51 g.) was added to a solution of absolute ether (300 ml.) and lithium aluminum hydride (8.9 g.) according to the method of Nystrom and Brown (10). The α-pentenal was distilled under nitrogen, b.p. 29°-31°C./10 mm. Yield 21.3 g.

The α-pentenal was prepared from the α-pentenol (21.3 g.) by the low temperature dichromate oxidation method of Delaby and Guillot-Allegré (1). The α-pentenal was extracted with diethyl ether and distilled under nitrogen in the presence of hydroquinone: b.p. 30°C./12 mm., yield 3.38 g. The aldehyde was identified by preparation of the semi-carbazone derivative, m.p. 172°-173°C. [m.p. 180°C. for α-pentenal semi-carbazone, Delaby (8)].

The 2,4-dinitrophenylhydrazone of the synthetic α-pentenal was chromatographically purified and crystallized once from 80% ethanol: m.p. 162°-163°C. *Anal. Calcd.* for $C_{11}H_{12}N_4O_4$: C, 50.3; H, 4.57; N, 21.19. Found: C, 50.1; H, 4.73; N, 21.10. The mixed melting point of the authentic α-pentenal DNPH and "soybean" α-pentenal DNPH was: 150°-151.5°C.

The absorption spectra of authentic α-pentenal DNPH and "soybean oil" α-pentenal DNPH were prepared to evaluate the degree of unsaturation and further establish the identity of the "soybean oil" α-pentenal DNPH. Studies of 2,4-dinitrophenylhydrazones by Roberts and Green (11) show that an increasing degree of conjugated unsaturation and increasing substitution of alkyl groups cause a shift of absorption maxima toward the longer wavelengths. While the latter effect is very small, the effect due to α,β-unsaturation of the carbonyl moiety of the DNPH derivative is considerable (amount 17 mμ).

Spectrophotometric curves of the authentic α-pentenal DNPH and "soybean oil" α-pentenal DNPH in ethanol are shown in Figure 4. The DNPH's of both preparation and isolation processes show very nearly similar curves with their maxima at 375 mμ and 376 mμ and minima at 313 mμ and 314 mμ.

Notably absent from the list of aldehydes isolated is α-heptenal (9). There are indications that it may be present in a minor band not yet characterized. Its

TABLE II

Soybean Oil Volatiles

↓

Adsorption Analysis

↓

(Silicic acid + filter-cel (1 + 1) + 5% florophors)
(5% ethanol in pentane-hexane)

Painty fractions

↓ Chromatography of DNPH (0.4128 g.)

P_B[1] acetaldehyde DNPH—93.3 mg., m.p. 164°C.

C_T	H_T	N_T	C	H	N
42.86	3.60	24.99	43.0	3.87	25.55

P_C[1] propionaldehyde DNPH—18.4 mg., m.p. 150°-152°C.

C_T	H_T	N_T	C	H	N
45.38	4.23	23.52	45.7	4.36	23.9

P_D[1] red band—5.8 mg.

P_E[1] hexanal DNPH—289.1 mg., m.p. 93.5°-95°C.

C_T	H_T	N_T	C	H	N
51.40	5.78	20.01	52.2	5.63	20.1

Rancid fractions

↓ Chromatography of DNPH (0.4467 g.)

R_B acetaldehyde DNPH—81.5 mg., m.p. 165°C.

C_T	H_T	N_T	C	H	N
42.86	3.60	24.99	43.3	3.84	25.2

R_C propionaldehyde DNPH (?)—67.5 mg., m.p. 141°-148°

C_T	H_T	N_T	C	H	N
45.38	4.23	23.52	46.4	4.43	23.2

R_D α-pentenal DNPH—82.8 mg., m.p. 149°-153°C.

C_T	H_T	N_T	C	H	N
50.30	4.57	21.19	50.8	5.01	21.6

R_E diffuse band—7 mg.

absence or low concentration may result from the low temperature of autoxidation and the low temperature at which the aldehydes were volatilized.

A schematic summary of the fractionation, isolation, and characterization data is given in Table II.

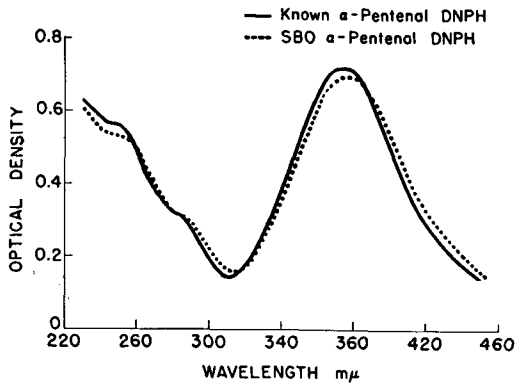


FIG. 4. Spectrophotometric curves for DNPH derivatives of a synthetic α-pentenal and of a fraction isolated from soybean volatiles.

Discussion

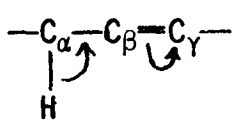
Previous work on the flavor problem of soybean oil has demonstrated that linolenic acid is the unstable precursor of the undesirable "reverted" flavors in soybean oil (2). Further, the deterioration has been shown to be oxidative (3). Studies on the initial oxidation products of pure methyl linolenate have shown that polymerization accompanied by cleavage occurs immediately (5) upon oxygen absorption and have led to the speculation that this cleavage product is an aldehyde.

Obviously not all the aldehydes formed in the autoxidation arise from linolenic acid which occurs to the extent of 9% in soybean oil. Any attempt to determine which aldehyde is responsible for the flavor or odor peculiar to soybean oil must meet at least two criteria:

1. The aldehyde must occur largely in the painty or reverted fraction.
2. It must be an aldehyde primarily formed in the oxidation of linolenic acid.

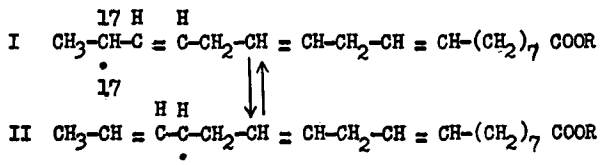
Unfortunately the evidence of the present paper is inadequate to answer the first criterion concerning the association of aldehydes and odors. Inspection of Table II shows that either the primary adsorption analysis of volatile aldehydes was only partially effective or that the selection of fractions for combining into the two components was not optimal. Acetaldehyde is present equally in painty and rancid components; propionaldehyde, α-pentenal, and crotonaldehyde occur in the rancid fraction while hexanal was isolated only from the painty fraction. It is apparent that the emphasis of future studies must be placed upon an improved preliminary fractionation of the volatile aldehydes prior to their identification as derivatives.

In consideration of the second criterion, acetaldehyde, propionaldehyde, crotonaldehyde, and α-pentenal would be given more consideration than α-heptenal and hexanal since their formation from linolenic acid can be rationalized by employing the hydroperoxide hypothesis of Farmer *et al.* (4); the last named was, in fact isolated from autoxidized cottonseed oil (15). Olefins containing the $-CH_2-CH=CH-$ system are easily autoxidized due to the enhanced reactivity of the hydrogen atom in the α-methylene group, which with the double bond forms a 3-carbon system. This reactivity may be explained by the existence of a hyperconjugative polarization. In the following system:

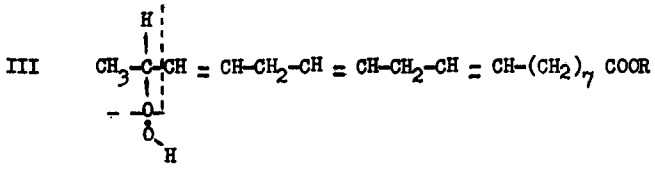


the hydrogen at α-carbon, which activation will facilitate the removal of a hydrogen atom by an active oxygen molecule in the para-magnetic state or by an active free radical fragment. The formation of acetaldehyde may be rationalized as follows. The abstraction of an H atom from the linolenate at carbon

position 17 will yield two resonating forms of free radical ester.

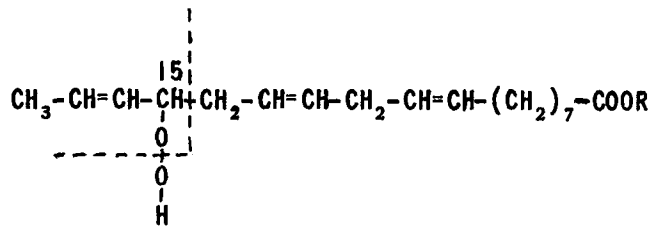


When form I reacts with a molecule of active oxygen, a peroxidic free radical of linolenate is formed which can further abstract a hydrogen atom from a nearby ester to form 17-hydroperoxide linolenate



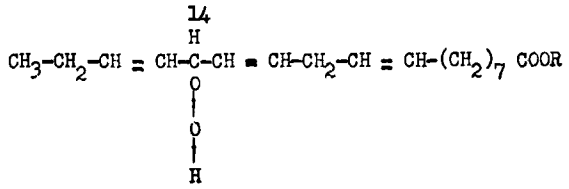
The homolytic scission of the O—O bond and the simultaneous cleavage of the adjacent C—C bond will yield acetaldehyde CH_3-CHO + an unidentified fragment HO—CH=CHR' (?).

Since form II is a second resonating structure, the following 15-hydroperoxide linolenate

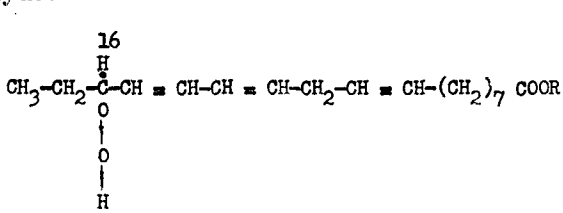


may undergo degradative decomposition to yield crotonaldehyde.

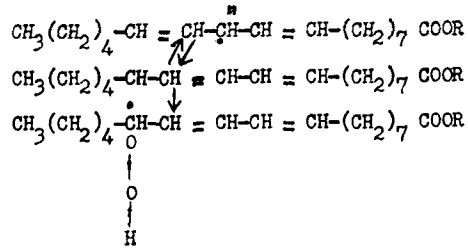
The formation of α-pentenal results from the degradative decomposition of 14-hydroperoxide linolenate:



Similarly, 16-hydroperoxide linolenate, resulting from the resonating structure, will yield propionaldehyde:



Hexanal can best be rationalized as a cleavage product of linoleate:



It will be apparent that many aldehydes suggested need now to be related to the flavor problem of soybean oil by organoleptic studies of the pure compounds. Further it is apparent that isolation of autoxidation products from pure methyl linolenate will also be useful in identifying the offending aldehyde or aldehydes. These suggested lines of work are the subject of current research.

Summary

Volatile odor principles of reverted soybean oil collected at very low temperature have been fractionated into rancidity and reversion components by adsorption on silica gel. These principles apparently contain aldehyde groups since they can no longer be detected organoleptically after the addition of aldehyde reagents.

Isolations of individual aldehydes within the rancid and reverted fractions were made by forming the 2,4-dinitrophenylhydrazones and chromatographically separating these colored derivatives. Identifications were based upon melting points, ultimate analyses, and adsorption data.

The following aldehydes were identified: acetaldehyde, propionaldehyde, α-pentenal, and hexanal. There is strong evidence that crotonaldehyde is also present although not completely resolved from propionaldehyde as dinitrophenylhydrazones.

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