unsaturated fatty acid groups, was also applied to our palm oil sample and the results obtained also show in Table V. As can be seen, there is a reasonable agreement between the results of the various analytical methods; however, data for two different samples of palm oil show in Table V.

Since the above chromatographic method constitutes a real fractionation without chemical transformation of the sample, all fractions thus obtained can be subjected to additional analytical investigation. For instance, enzymatic hydrolysis with pancreas lipase, which gives information about the distribution of the fatty acid composition in the α- and β-positions, can be applied.

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Soybean Unsaponifiables: Hydrocarbons from Deodorizer Condensates

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Abstract

Molecular distillation of deodorizer condensates followed by chromatography on alumina, gave substantial quantities of hydrocarbons free of other unsaponifiable constituents. Squalene comprised 50% of the hydrocarbon fraction and contained practically all the unsaturation. A crystalline, saturated hydrocarbon fraction of 4.2% was composed primarily of C_{29} and C_{31} paraffins. An unresolved fraction was composed of two major components, each estimated to contain about 30 or 35 carbon atoms. Minor amounts of many hydrocarbons with chain lengths of 15–35 carbon atoms were present but not completely identified. C^{14} analysis showed that the hydrocarbons are natural to soybean oil and they are not artifacts arising from petroleum solvent residues.

Introduction

SATURATED, UNSATURATED and terpenoid hydrocarbons have been reported as constituents of the unsaponifiable fractions obtained from vegetable oils (1,5,8,10). Hydrocarbons constituted the bulk of unsaponifiable matter in deodorizer distillates obtained from peanut, cottonseed, sunflower and palm oils (8). The even-numbered carbon chains so common to fatty acids are not observed in unsaponifiable hydrocarbons. Nor does the hydrocarbon chain length appear to hold any relationship to the molecular size of the component fatty acids. Aliphatic hydrocarbons from C_{13} to C_{52} have also been reported as unsaponifiable constituents (8,9).

Usually strong odors are not associated with hydrocarbons, but Marcelet (9) reports an agreeable aromatic odor for a $C_{13}H_{24}$ diene hydrocarbon obtained from olive oil and strong odors and a nauseating taste for two unsaturated hydrocarbons obtained from peanut oil. Jasperson and Jones (8) concluded from their examination of deodorizer distillates from six vegetable oils that the predominant type of hydro-

carbon was terpenoid, which possessed a strong odor and nauseating taste. Their study did not include soybean oil. However, chromatographic curves published by Cappella et al. (1) indicate that the composition is similar to that of other vegetable oils. Our previous publication indicated that only the hydrocarbon portion of unsaponifiables contributed to the flavor problem of edible soybean oil (7). Hydrocarbons from soybean unsaponifiables have not been thoroughly
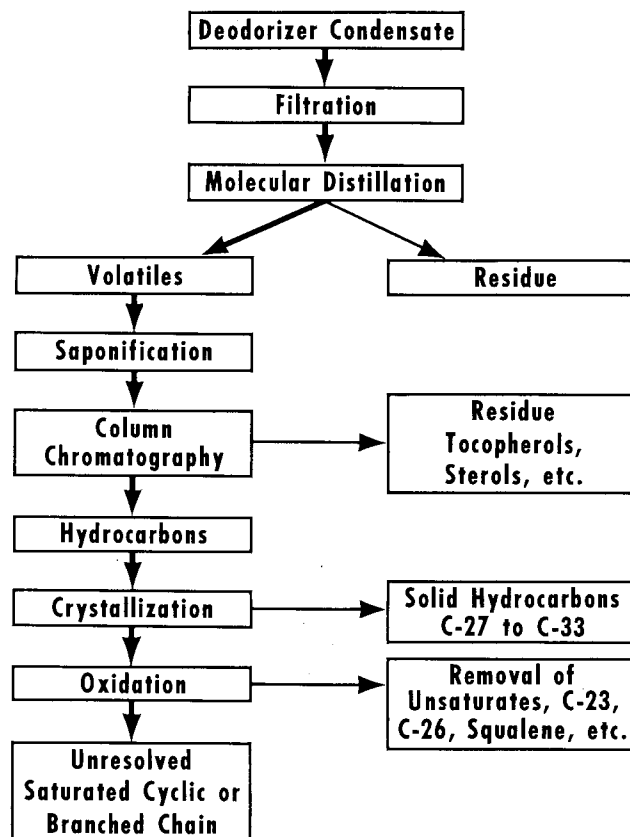

FIG. 1. Flow sheet for fractionation of deodorizer condensate.

Sample	Temp C	Pressure mm Hg	Volatile	Unsaponi- fiable in volatile	Hydro- carbon in sample
			%	%	%
SDC 1 [a]	200	0.03	14	85	1.4
SDC 2	240	0.15	16	13	0.4
Clabber 3	195	0.04	50	78	3.4

[a] Shell drain condensate.

characterized, although squalene $C_{30}H_{50}$ (5) and ga- dusene $C_{18}H_{32}$ (10) have been reported as consti- tuents of soybean oils. This paper reports isolation and characterization studies made on the hydrocar- bon fraction of unsaponifiables obtained from a com- mercial soybean oil deodorizer distillate.

Material and Methods

Source materials for the isolation of hydrocarbons were a) the shell drain concentrate from a Girdler deodorizer, b) the shell drain concentrate and c) the hot-well skimmings or "clabber" from a Blaw-Knox deodorizer. These materials are referred to as deodor- izer condensates. Figure 1 outlines the fractionating procedure used to obtain the hydrocarbons from the deodorizer condensate unsaponifiables. Molecular dis- tillation data, obtained on an Asco No. 50 Rota-Film still, show in Table I. The volatile fraction was saponified twice, and the yield of unsaponifiables and hydrocarbons is based on wt of starting material.

Alumina chromatographic columns, packed into either Woelm or regular chromatographic alumina Harshaw AL-0102-P, were equally satisfactory in sep- arating the hydrocarbon fraction from other unsaponi- fiable components (2,14). Columns were developed with petroleum ether; if fractions beyond the hy- drocarbons were desired, the mixtures of petroleum ether and diethyl-ether were used. Columns of Darco decolorizing carbon were used to fractionate the satu- rated hydrocarbons from the unsaturated. These columns were eluted with petroleum ether, and the separations obtained were followed by gas chromatog- raphy and thin-layer chromatography (TLC).

Gas-liquid chromatographic analyses were con- ducted on a 4-ft silicone gum-rubber column operated up to temp of 270C. Thin-layer chromatograms were made with 9 parts Mallinckrodt 100-mesh silicic acid and 1 part plaster of Paris; these were developed in a 10% diethyl ether-pentane mixture.

Tosylations and brominations were conducted in the usual manner (13). Oxidation of the unsatuated hy- drocarbons was conducted in acetone containing 10% water, with $KMnO_4$ (13). The resulting mixture was separated on alumina to recover the saturated hy- drocarbons.

The following hydrocarbons, which are available from various commercial sources, were used as chro- matographic standards: n-decane, octadecane, 1-octa- decene, n-octacosane (containing C_{26} and C_{30}), dotri- acontane (containing C_{28} and C_{30}), tetratriacontane, squalene, and squalane.

Results

Deodorizer condensates were warmed and filtered hot to remove extraneous materials such as dirt and lint and to obtain a clean, dry product that could be molecularly distilled. Data in Table I show com- positions of shell drain condensates (SDC) from two different types of deodorizers now in current use. Op- erating conditions of the commercial deodorizers (4) undoubtedly account for differences in the amount
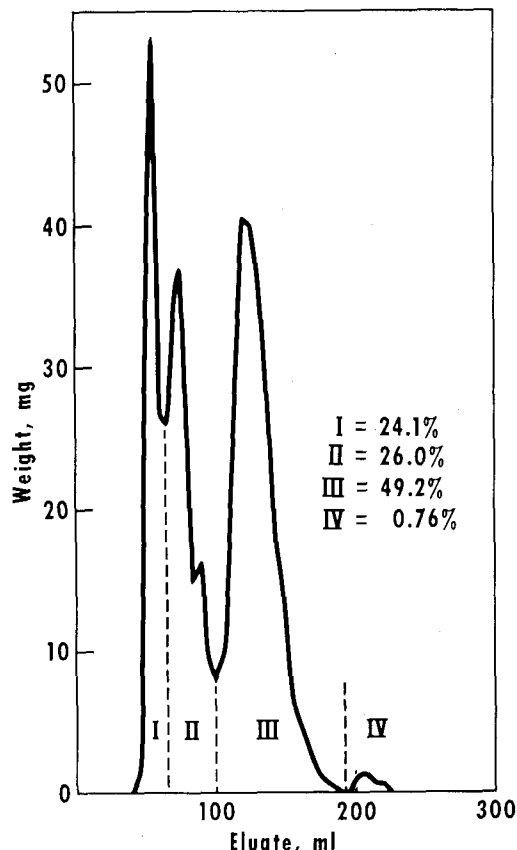

FIG. 2. A silicic acid liquid-liquid chromatogram of un- saponifiables from the volatile portion (195C at 4 μ) of dis- tilled hot-well clabber, I = hydrocarbons, II = various tocoph- erols plus unknowns, III = sterols, IV = highly polar materials.

of volatile materials in the two samples. At 200C practically no volatile material came from SDC 2, and when the temp was raised to 240C, a volatile fraction was obtained but the amount of the hydro- carbon fraction was small (0.4%). TLC indicated that practically all the hydrocarbons in SDC 2 were in the volatile fraction; however, at the lower temp of distillation (200C) employed on SDC 1, TLC tests indicated that a considerable amount of hydrocarbons was retained in the residue fraction. Because of low yield further studies for the isolation of hydrocarbons were not conducted on the SDC 2 sample. The hot- well clabber gave the highest yield of volatile prod- uct (50%) and also the highest yield of hydro- carbons (3.4%).

A silicic acid liquid-liquid chromatogram (Fig. 2) shows that the composition of clabber unsaponifiables is very similar to the unsaponifiable obtained from SDC and soybean oil (6,7). Figure 3 shows the TLC of samples taken at midpoint of each of the peaks in Figure 2. Identification of the spots with known materials, except peak IV which is an orange-colored band of highly polar material (probably oxidative polymer), shows the major fractions to be hydro- carbons, tocopherols and sterols. Concn and crystal- lization of the tosylates produced a filtrate high in hydrocarbon content (6). A quantitative separation of the hydrocarbons, indicated by TLC and IR, was obtained on an activated alumina column. The suc- cess of this separation prompted examination of the unsaponifiables directly upon an activated alumina column.

Yields of 8.8% hydrocarbons were obtained from the unsaponifiable volatile fraction of the clabber. Be- cause of the high polarity of the sterols and tocoph-
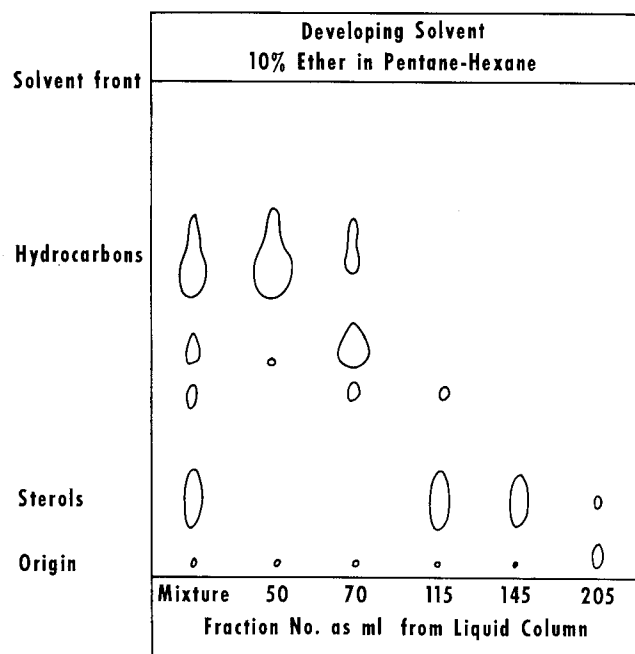
FIG. 3. Thin-layer chromatogram of fractions taken from a liquid column of the saponified volatile fraction of hot-well clabber.

erols, large amounts of unsaponifiables (8.0 g) can be successfully chromatographed on relatively small amounts (100 g) of activated alumina. Long tailing was exhibited by these columns probably because of the large amount of sample employed, and this tailing necessitated taking many eluate fractions. The purity of the fractions was followed by TLC.

A bromine test and an IR examination indicated an abundance of unsaturation in the hydrocarbon fraction. The hydrocarbons were examined by GLC on a silicone gum-rubber column, at temp up to 270C. Tentative identification, by log-log plots and against known hydrocarbons, indicated that many compounds were present, within a carbon chain range of C_{15} to C_{36}. The majority of the material had chain lengths in the neighborhood of 30 carbon atoms. Since the major quantity of the hydrocarbons had chain lengths greater than the pentane-hexane distillation residues and contained unsaturated materials, it would seem that these products are native to soybean oil and are not contaminating materials derived from hexane-
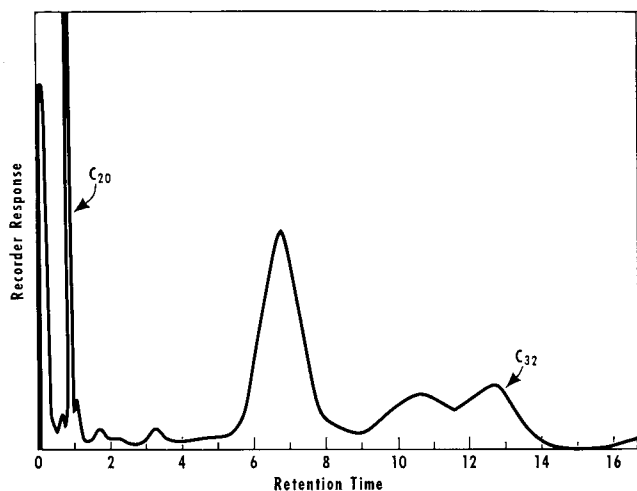

FIG. 4. Gas-liquid chromatogram of the hydrocarbon fraction obtained from hot-well clabber. Known C_{20} and C_{32} hydrocarbons added as standard reference materials. A 2-ft 3% silicone gum-rubber column was operated at 270C.
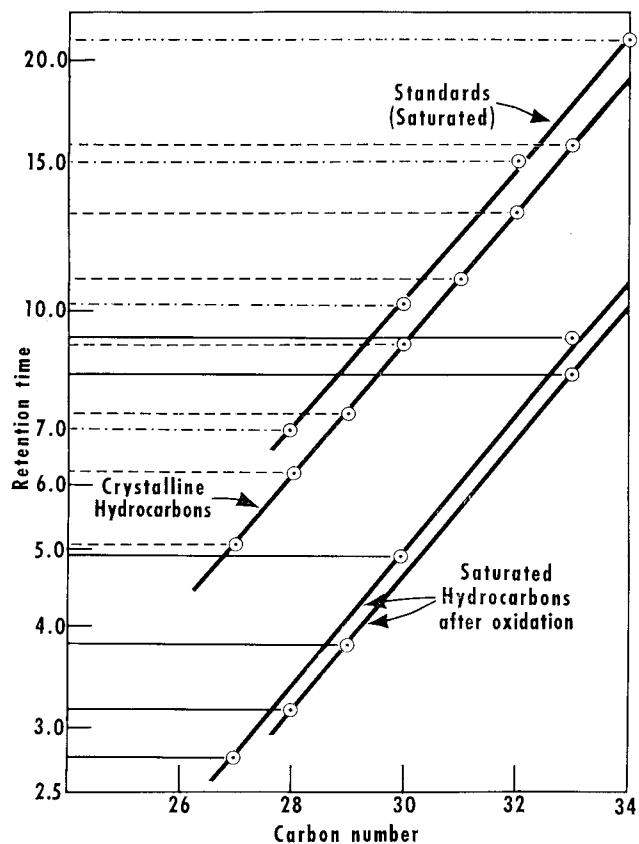

FIG. 5. Log retention time for hydrocarbons from soybean oil, shell drain concn plotted against carbon number. Plots are from three isothermal gas chromatographic runs on a silicone rubber column in which temp (300-330C) was held constant but set differently for each run.

solvent residues. Figure 4 shows the gas chromatogram of the hydrocarbon fraction obtained from a deodorizer distillate. Three components at approximate carbon numbers C_{30}, C_{31}, and C_{32} constitute 50, 20, and 20%, respectively, of the total hydrocarbons present.

Figure 5 shows the log retention time versus the carbon number plots for hydrocarbons obtained from soybean oil, SDC 1. The presence of at least four types of hydrocarbons is indicated by Figure 4 (3). Hydrocarbons present in SDC could include a) saturated crystalline hydrocarbons (C_{27} to C_{32}); b) unsaturated hydrocarbons, i.e., those removed by oxidation which could be aliphatic, branched chain or cyclic; c) the terpenoid type and possibly its saturated counterpart; and d) saturated branched chain or cyclic material. The whole hydrocarbon mixture, even after removal of the crystallizable saturates, is too complex to be resolved by gas chromatography without prior fractionation. The two identity lines shown at lower right in Figure 5, indicate that at least two types of noncrystallizable saturated hydrocarbons are present (3). The identity of these hydrocarbons has not been established.

Squalane and squalene, because of their branched structure, have shorter retention times than normal hydrocarbons and are equivalent, on a silicone column, to a C_{28} and a C_{29} saturated hydrocarbon, respectively. Although squalene can be removed by oxidation, a small amount of hydrocarbon having the same retention time remains in the oxidatively stable portion of SDC. Preliminary studies with mass spectra for hydrocarbons of this mol wt have not been helpful because of the lack of strong parent peaks and be-
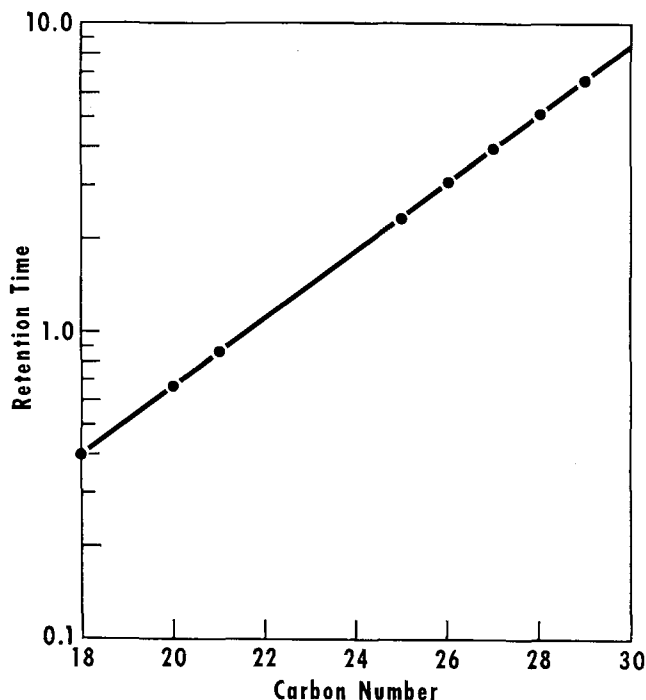
FIG. 6. Log retention time plot against carbon chain length of hydrocarbon standards.

FIG. 7. Gas chromatogram of A. saturate crystalline hydro-carbons from SDC 1 unsaponifiables, and B. same sample with added hydrocarbon standards.

cause of the presence of the large number components in the mixture.

The silicone columns as normally employed in GLC do not distinguish between saturated and monoun-saturated materials, although the multibranched chain and iso compounds have a retention time lower than normal alkane hydrocarbons. Thus the tentative iden-tity plot for an unknown C_{30} carbon compound could easily be in error by 1 or 2 carbon atoms. For this reason, plus the inherent error for high temp opera-tion, as many known standards as possible in the C_{20} to C_{34} range were included in this work. Figure 6 shows the relationship of the retention times (at 270C) to carbon number of these known materials. The good linear agreement between carbon number and the log of the retention time indicates that the method is applicable to these high-boiling (200–300C) materials.

Crystalline Hydrocarbons. The first fractions eluted from the alumina column, when stripped of solvent, developed crystals upon standing. These crystals were collected and recrystallized from absolute etha-nol. A yield of 4.0–4.2% of the total hydrocarbon fraction was obtained. Carbon-hydrogen analysis showed 85.04% carbon and 14.69% hydrogen, indi-cating a pure hydrocarbon. IR analysis showed nothing but evidence of a straight chain hydrocarbon. The crystals gave a negative bromine test, also a negative Libermann-Burchard test. Although the crystals melted sharply at 67.5C, the gas chromato-graphic analysis (Fig. 7) showed the presence of 65% hentriacontane, 8% triacontane and 27% nonacosane, plus a trace of heptacosane, octacosane, dotriacontane and tritriacontane.

Unsaturated Hydrocarbons. The bromine test indi-cated a large amount of unsaturation in the original hydrocarbon fraction; however, attempted crystalliza-tion of the bromides was not successful. Oxidation of the mixture with potassium permanganate in ace-tone completely removed the unsaturated components. The oxidized mixture was chromatographed through alumina to remove any glycols. GLC analysis before and after oxidation showed the removal of the largest
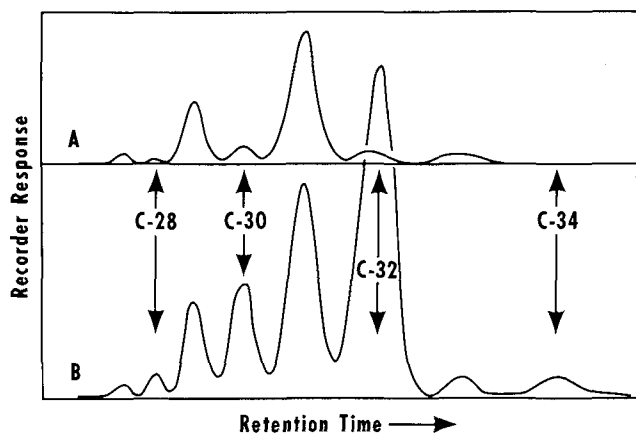
peak, identified as squalene, and two smaller peaks in the C_{23} and C_{26} carbon region. The remaining peaks retained the same elution position, including eicosane which was used as a reference standard.

Squalene identification was confirmed by hydro-genation of the mixture with a 10% palladium-on-charcoal catalyst. The odor of the sample disap-peared upon hydrogenation and the position of the GLC peak shifted from that of squalene to squalane. Good agreement was obtained between the observed bromine uptake and that calculated for squalene. The squalene content has been estimated from the various GLC determinations as constituting 50% of the hy-drocarbon mixture. Squalene has been reported as a natural constituent of all vegetable oils except cocoa butter (2,5,8,14).

Squalene can be obtained in approximately 95% purity by chromatographing the entire hydrocarbon
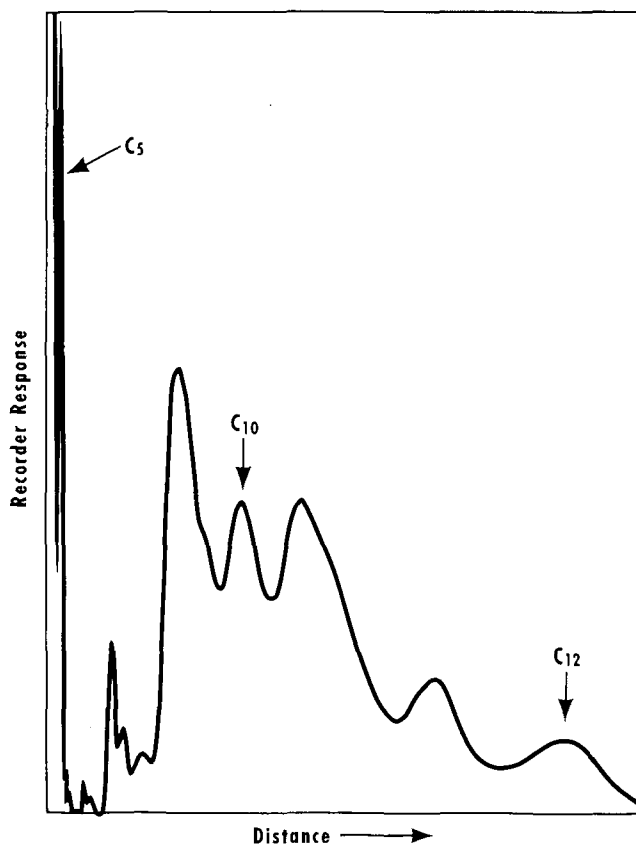

FIG. 8. Gas chromatogram of petroleum-ether residues, a low-boiling fraction. Silicone column isothermal run at 75C.
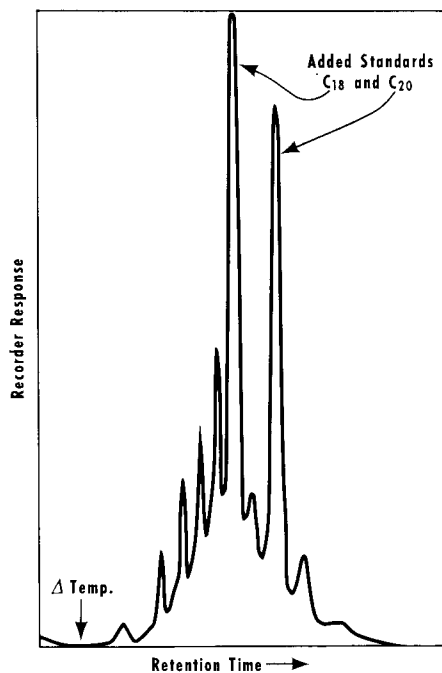
FIG. 9. Gas chromatogram of high-boiling fraction. This chart is a continuation of Figure 8 but with temp programmed at the point indicated. Known C_{18} and C_{20} hydrocarbons added as standards.

FIG. 10. Gas chromatogram of crystalline hydrocarbons obtained from paraffin wax. Silicone column 300C.

mixture through a column of activated carbon. The unsaturates are the first major components to be eluted, and check chromatographic runs with knowns showed that 1-octadecene and eicosane can be separated and a substantial part of the olefin obtained in pure form before the saturates are eluted. Preliminary tests with the saturated soybean crystalline hydrocarbons (mostly C_{29} and C_{31}) indicate that some fractionation can be obtained according to chain length. In this mixture, the major portion of C_{29} was obtained completely free of the C_{31} component.

Saturated Liquid Hydrocarbons. The liquid hydrocarbon fraction, obtained after removal of the crystalline components and the unsaturates, has not been resolved or crystallized. GLC results indicate there are two major components in amounts of ca. 20% each which, judging from retention times, will have carbon chain lengths in the region of C_{30} to C_{35}.

Judging from their properties, it is quite possible that they are branched chain hydrocarbons.

Residues from Pentane-Hexane Solvents. Although specifications for extraction solvents (12) show a min a high-boiling components, a considerable amount of residue was found in the laboratory-supplied pentane-hexane. The petroleum ether used throughout this work was redistilled before use. Distillation of three pentane-hexane solvents at atmospheric conditions showed 0.15,0.07 and 0.05% residue material, which had bp above 100C. Complete distillation of the residue was not attained at 120C under vacuum of 0.1 mm. Figure 8 shows an isothermal gas chromatographic curve of the low-boiling constituents; Figure 9 is the temp programmed continuation of the same run showing the high-boiling components in the pentane-hexane residues. Standard hydrocarbons C_{18} and C_{20} were added to the mixture as an aid in identifying the carbon chain lengths of residue material. High mol wt components may be present, but the indications are that C_{22} hydrocarbons are about the upper limit; as indicated previously, these are shorter chain lengths than the hydrocarbons in soybean unsaponifiables. The evidence would indicate
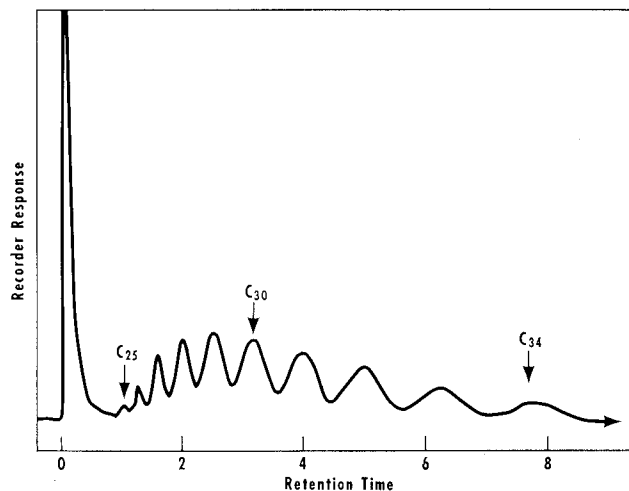
that such hydrocarbons are native to soybean oil and are not contaminates arising from extraction solvents used in the processing of soybean oil.

Paraffin wax can be readily crystallized from acetone to yield saturated hydrocarbons containing C_{24} and C_{34} components in about equal amounts. Figure 10 shows the gas chromatogram of the crystallized components obtained from paraffin wax. The comparative ease with which the paraffin wax crystallized would probably indicate that the major part of the saturated soybean unsaponifiables does not consist of straight chain hydrocarbons. The figure of 4.0% saturated hydrocarbon components in soybean unsaponifiables is somewhat substantiated by these observations.

Possibly hydrocarbons of chain lengths greater than tetratriacontane may also be present in soybean oil unsaponifiables and deodorizer distillates. However, because of their higher bp and lower vapor pressures it would not be possible to detect and isolate them under the conditions employed in this study. Jasperson and Jones (7) reported monounsaturated C_{52} hydrocarbon (6%) present in unsaponifiables from palm oil deodorizer distillates. They also report the presence of a highly unsaturated C_{40} hydrocarbon (4%) in peanut oil deodorizer unsaponifiables.

Carbon C^{14} analysis would indicate the source of hydrocarbons in solvent-extracted vegetable oils (11). Hydrocarbons arising from plant sources have a C^{14} count (12–14 cpm/g.), whereas those originating from petroleum sources have a zero count; mixtures show proportional values. Although the petroleum solvent residue values reported by Ryder et al. (12) are extremely low and although the analysis of laboratory hexane-pentane solvent residues would indicate that dewaxing removes hydrocarbons above C_{24}, the problem of contamination is ever present.

Table II shows the results of C^{14} analysis on samples of unsaponifiable hydrocarbons from deodorizer condensates (clabber), squalene, soybean oil, pentane-hexane, and pentane-hexane residue. C^{14} activity was determined by liquid scintillation counting and the specific activity of the fractions were compared to that of soybean oil. Samples were counted for 150 min each and total counts of 3,500–10,000 were obtained. The specific activity was determined by counting weighed samples and recounting after the addition of a known amount of C^{14} in order to determine the efficiency of counting. A background vs. efficiency curve was established for several quantities of petro-

TABLE II
Contamination of Unsaponifiables as Determined by Carbon-14
Analysis for Petroleum Residues

Sample	Counts min	Effi- ciency	cpm/gr sample	Esti- mated contami- nation
		%		%
Soybean oil	33	32.0	13.9	0
Unsaponifiables				
Hydrocarbons	8	16.0	18.2	0
Hydrocarbons	10	31.4	10.2	20
Hydrocarbons	11	36.5	11.2	20
Squalene	40	45.9	11.8	25
Pentane-hexane	0	56.7	0	100
Pentane-hexane residue	0	9.7	0	100

leum oil and this background used to correct the counting rate of the samples.

Possible contamination of the unsaponifiable hydrocarbon samples by petroleum solvent residues varied from 0 to a possible 20%. These values apparently vary within the limits of accuracy of the method as would be indicated by the squalene control sample. C^{14} counts for soybean oil and the petroleum solvent and residue showed the expected counts. Thus, hydrocarbons isolated from soybean oil deodorizer condensates are native to soybean oil and did not arise from petroleum solvents used to process the oil.

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On the Polarographic Behaviour of the Palmitates and Myristates of Copper and Cobalt

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Abstract

Pyridine complexes of myristates and palmitrates of copper and cobalt were found to be reducible at the dropping mercury electrode in 1) LiCl in 1:1 benzene methanol mixture; 2) MeHSO$_4$ in 1:1 benzene methanol mixture; and 3) KCl in glycol. The diffusion current was found to be a linear function of concentration. Hence it was concluded that this linear relationship can be successfully employed for the estimation of cobalt and copper concentration in their respective soaps.

Introduction

THE COMPLEX formation between pyridine and heavy metal soaps was pointed out by Boner (1). Recently we have done some preliminary experiments to study the polarographic (3) and spectrophotometric (4,5) behaviour of some metal soaps. It was found that these methods can be employed for the quantitative estimation of metal ions in the soaps. Due to these encouraging results it was thought worth-while to extend these studies to some other soaps such as those of cobalt and copper. The present communciation deals with the polarographic behaviour of myristates and palmitates of copper and cobalt in various nonaqueous media.

Experimental

Reagents. Palmitic and myristic acids were B.D.H, C.P. grade, used after fractionation under reduced pressure for the preparation of sodium soaps. The

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metal salts of copper and cobalt, pyridine, potassium chloride, lithium chloride and methyl red were B.D.H, A.R. grade. Benzene, methanol and glycol were used after extensive purification and careful drying. Triple distilled A.R. mercury was used for polarographic measurements.

Preparation of Metal Soaps. The soaps were prepared (2) by precipitation method, adding an equivalent amount of hot dilute cobalt or copper salt solution to an equivalent amount of hot dilute sodium palmitate or myristate under vigorous stirring. The precipitated soap was filtered, washed thoroughly with hot water followed by dry acetone and ether and dried in a vacuum desiccator. The copper content of the soap was found by ashing a known amount of the soap, dissolving the ash in mineral acid and titrating the copper iodometrically; the metal content was 10.98% for the palmitate [calculated for Cu $(C_{15}H_{31}COO)_2$ 11.08%] and 12.13% for the myristate [calculated for Cu$(C_{13}H_{27}COO)_2$ 12.20%]. The cobalt soaps were subjected to similar treatment and the amount of cobalt determined gravimetrically. Metal content was 11.12% for the palmitate [calculated for Co$(C_{15}H_{31}COO)_2$ 11.49%] and 10.20% for the myristate [calculated for Co$(C_{13}H_{27}COO)_2$ 10.36%].

Apparatus and Technique. The polarographic technique applied here was the same as described earlier (3). Supporting electrolytes and the solvents used were the same as in the case of nickel soaps (3). Methyl red (0.004%) was used as the maximum suppressor in 1:1 benzene-methanol mixture in the case of methyl hydrogen sulphate as supporting electrolyte. The capillary constant $m^{2/3} t^{1/6}$ was 1.618, 1.320, and