or in combination with BHA or BHT, produces the highest stability in lard. When used alone, it reaches its maximum efficiency at about .02% and decreases thereafter. BHT produces fairly high AOM values at high concentrations but would not be comparable to propyl gallate at food-approved concentrations of .01% and less. BHA at low concentrations is about equal to BHT but reaches its peak effectiveness at about .010%. Higher BHA concentrations apparently have little effect on the AOM stability of lard. The combination of BHA and propyl gallate produces higher AOM's than the combination of BHT-propyl gallate. This indicates that there is synergism between the BHA and propyl gallate at all concentrations tried but little or no synergism between BHT and propyl gallate. The combination of BHA and BHT shows a slight synergism from the AOM standpoint, but more work should be done before definite conclusions are made.

BHA alone produces the best carry-through stability at food approved concentrations. BHT, while not as good at lower concentrations, produces higher stability at concentrations above .02%. Propyl gallate is approximately equal to BHT in carry-through as tested in potato chips but apparently will not stand the high baking temperatures of either pastry or crackers. The efficiency of the synergistic mixtures containing propyl gallate is good in the case of potato chips, but when higher temperatures are used, as in the case of crackers and pastry, the BHA-BHT combination is better than either of the other two. It is believed that the marked difference in the carry-through effect of the various antioxidants in pastry as compared to crackers is due to the higher fat content used in pastry. These data as well as other work at this laboratory have shown that carry-through data in pastry is usually more concise and clear-cut than the same data in crackers.

These data indicate that combinations of BHA and propyl gallate produce the best stability in lard if used at limits authorized by the Meat Inspection Branch. If only AOM stability is considered, propyl gallate alone is the best antioxidant. If carry-through stability alone, especially at higher temperatures, is the chief qualification, then the best antioxidant is a combination of BHA plus BHT.

Summary

Butylated hydroxyanisole, butylated hydroxytoluene, and propyl gallate were compared for antioxidant efficiency alone and in combination with each other in lard. A comparison of the physical properties of these three antioxidants was also made.

BHA was found to synergize with propyl gallate to produce the best all-around antioxidant. The mixture of BHA and BHT produced the best carry-through stability in lard, particularly when higher temperatures were used. Propyl gallate alone produces the best AOM stability in lard.

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[Received November 12, 1954]

Investigations on the Bitter and Beany Components of Soybeans[1]

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SOYBEAN FLOUR contains substances that impart undesirable bitter and beany flavors and odors to soybean food products. Although many minor constituents of the soybean have been identified, none has been shown to be responsible for these bitter and beany flavors and odors. In fact, no investigations directed toward this specific purpose appear to have been carried out.

Horvath (4), referring to work by Schmalfuss and Treu (10), made the statement that methyl *n*-nonyl ketone is responsible for the beany flavor. This substance was however isolated from a sample of soybean oil rather than from the flour. No experimental evidence is presented to show that this ketone contributes to the flavor or odor of soybean flour.

A large number of patents covering processes for "debittering" soybeans are in existence. These processes are empirical, and there appears to be no available evidence that they are based on knowledge of the chemical nature of the beany or bitter principles. It is believed that if this knowledge were at hand, it would be possible to devise more satisfactory debittering processes and thus to obtain edible soybean products having no objectionable flavor. This paper is a report on the progress made in studying this complex problem.

In any study of the minor constituents of a natural entity, such as the soybean, one of the more perplexing problems is that of obtaining an extract or concentrate of the minor constituents that will be suitable for detailed organic chemical investigation and analysis. Beckel (2) had observed that when ethanol was used to extract oil from soybeans, the resulting flour contained less bitter and beany flavor than did flours prepared by other means. It therefore appeared that if the oil were extracted from the beans with hexane, in which the odor and flavor substances were not very soluble, and if the flakes were then extracted further with ethanol, the resulting alcoholic solution should contain many of the minor constituents that are responsible for flavor and odor.

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[1] Presented at the Paul Bunyan meeting of the American Oil Chemists' Society, Minneapolis, Minn., October 11-13, 1954.

A large quantity of an alcoholic solution obtained in the manner just described was available to us as a result of other investigations carried out at this laboratory. This solution, hereafter referred to as "alcoholic extract," was selected as a suitable starting material for investigation of the odor and flavor substances.

Before the results obtained in fractionating and analyzing this alcoholic extract are described, it should be made very clear that the isolation of a particular chemical compound from this extract does not necessarily mean that this compound existed as such in the original soybean. During extraction of the hexane-extracted flakes with 95% ethanol, alcoholysis, hydrolysis, or esterification reactions might occur. Carboxylic acids, if present originally in the flakes, might be isolated as ethyl esters. Complex esters might be hydrolyzed to free alcohol and acid, and the latter converted to an ethyl ester. Aldehydes and ketones might turn up as acetals. These are some of the changes that might be induced through the reactivity of the ethanol. Absolute proof of the original existence of a specific chemical compound in the bean would require very lengthy research involving the use of other methods of extraction and concentration, fractionation and analysis of the products, and correlation and interpretation of the results. Nevertheless fractionation and analysis of the alcoholic extract should give much useful information on the basic organic radicals from which the odor and flavor constituents must have been constructed.

Preliminary Processing of the Alcoholic Extract

The alcoholic extract was a clear brown solution having a pronounced beany odor. It contained approximately 120-130 g. of dissolved solids per gallon of solution. The solution was concentrated to a syrup by evaporation of ethanol in a vacuum evaporator. About 33 lbs. of syrup were obtained from 55 gal. of extract. This syrup was used without further treatment for investigation of bitter-tasting components. Volatile substances having a strong beany odor were isolated from the syrup by prolonged steam distillation. Approximately 100 hrs. were required to achieve substantially complete removal of odor bodies from 5.5 kg. of syrup. The slowness with which the odor bodies were removed suggests that they were being formed progressively, perhaps by hydrolysis, during the steam distillation. Certain experiments, described later in this paper, seem to confirm this viewpoint. The steam distillate was extracted with a mixture of equal volumes of ether and petroleum ether, and the ether solution was dried and evaporated, yielding about 0.3 g. of beany-odor bodies per gallon of original extract. Functional group analyses on the composite beany volatile fraction were:

Sap. value, 241; acid value, 142.5; carbonyl oxygen, 8.4%; iodine value, 42.3.

Qualitative tests for nitrogen, sulfur, and halogens were negative.

Investigation of Bitter-Tasting Components

The syrup obtained by concentration of the alcoholic extract was subjected to various methods of fractionation. The effect of fractionation on the concentration of bitter-tasting substances was determined by submitting samples of each fraction to a taste panel for evaluation.

The most efficient procedure for concentration of bitter-tasting substances was found to be fractional precipitation from ethanol or acetone. Bitter substances remained in the fraction most soluble in the solvent and could not be precipitated from solution even by chilling to —60°C.

A flowsheet for a typical fractional precipitation is shown in Figure 1. In addition to the separations shown in Figure 1, fractions B-2 and B-3 were submitted to additional fractionations, but no fraction having a bitter taste was obtained. Because fraction B-3 retained solvent tenaciously, no weight is reported for this fraction.

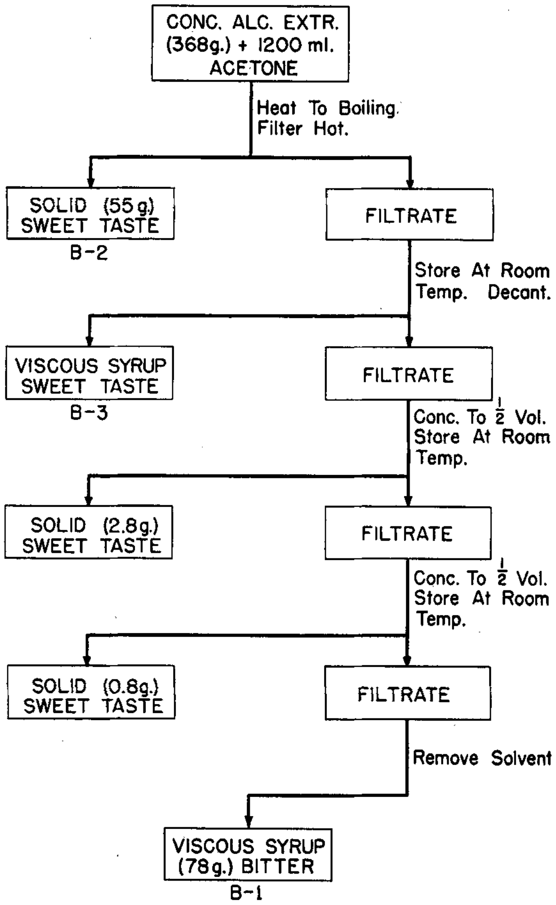

FIG. 1. Fractionation of bitter substances from alcoholic extract.

Saponification of fraction B-1 (5 g.) gave 2.5 g. of saponifiables having a saponification value of 188.5 and containing 88.2% of fatty acid, calculated as oleic acid. The unsaponifiable fraction (1.4 g.) was separated into 0.1 g. of a white, tasteless powder and a viscous residue. None of the materials isolated from the saponification had a bitter taste.

Fraction B-1 was further separated by dispersing a sample in water and extracting with hexane and ether, as shown in Figure 2. Stubborn emulsions were encountered during these operations. Centrifugation broke the hexane emulsions, but ether gave an emulsion layer which we could not break. The moderately bitter taste of the solid (B-5) isolated from this emulsion is probably due to incomplete separation from the aqueous layer containing the bitter substances (B-4).

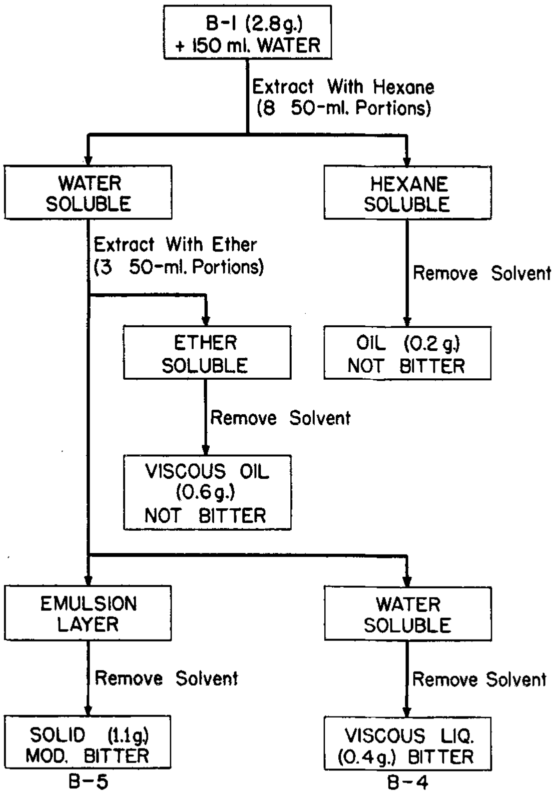

Fig. 2. Fractionation of bitter concentrate (B–1).

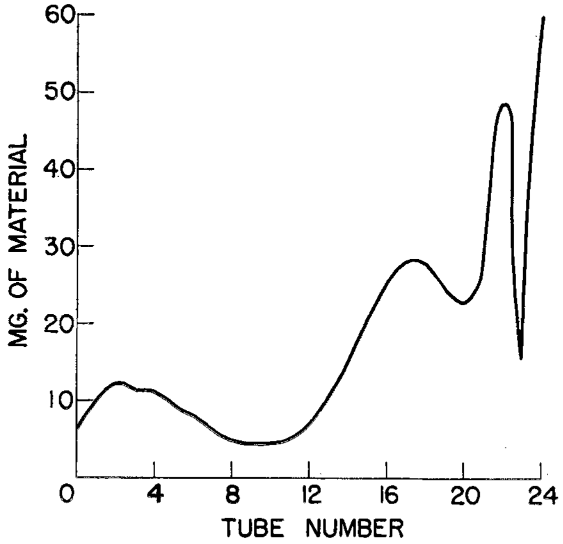

Fig. 3. Countercurrent fractionation of steam-volatile beany material.

Fraction B-4 gave the following results on analysis:

N, 0.93%; P, 1.89%; reducing sugar before acid hydrolysis, 12.9%; reducing sugar after acid hydrolysis, 9.2%; and sap. value, 132.

Reducing sugars were determined by the method of Somogyi (12), and the results are expressed in terms of galactose. Fraction B-4 was judged to be more bitter than fraction B-1.

Fraction B-4 is obviously not a pure substance. The observed nitrogen:phosphorus ratio indicates the presence of some phosphatidic material. The effect of acid hydrolysis on the amount of reducing sugars present appears to indicate the absence of glycosides. Attempts to obtain a bitter-tasting material by extraction of soybeans and soybean flakes with water were not successful. This failure suggests that the bitter component of fraction B-4 is not the same as that responsible for the bitter taste of soybeans or soybean flakes. It was observed that fractions rich in carbohydrates, obtained during fractionation of the alcoholic extract, underwent a browning or caramelizing reaction at temperatures as low as 40° to 60°C. Therefore fraction B-4 may owe its bitter taste to the presence of products of the browning reaction.

Investigations of the Beany-Odor Components

Countercurrent Distribution. To obtain a preliminary idea of the complexity of the volatile beany material, a sample was distributed between 80% ethanol and petroleum ether in a 24-tube metal Craig countercurrent-distribution apparatus (3). The weight curve, given in Figure 3, shows four fractions. The most polar fraction (tubes 0-10) had a burnt odor, the fraction of intermediate polarity (tubes 11-20) possessed a grassy, weedy odor, while the least polar materials (tubes 21-23 and tube 24) had an odor resembling rancid oil. Tubes 2, 17, 22, and 24 were tested with 2,4-dinitrophenylhydrazine for carbonyl materials according to the method of Lappin and Clark (6). All fractions examined gave a positive test which consisted of the development of a wine-red color. Tube 24 gave a weak test. The grassy, weedy material (tubes 14-19) was reprocessed in a countercurrent extractor having 50 tubes, but further resolution of components was not obtained.

Carbonyl Compounds. About 1 g. of beany volatile material was treated with 2,4-dinitrophenylhydrazine containing a little HCl and heated 15 min. on a steam bath. The 2,4-dinitrophenylhydrazones were obtained as a semisolid red material. This material was chromatographed on a 45 x 200-mm. column using silicic acid-Celite[2] (2:1) as an adsorbent. Petroleum ether-ethyl ether (3-8% ethyl ether in petroleum ether) was used as a developer. The resulting bands were rechromatographed on appropriate smaller columns until chromatographic homogeneity appeared to have been achieved. Many of the eluted bands were either oil or micro-amounts of crystals. Three crystalline materials were finally obtained in sufficient amount for analysis. On the basis of nitrogen, carbon, and hydrogen analyses, these substances appeared to be C-3, C-4, and C-5 carbonyl compounds. X-ray studies on the C-3 and C-5 materials led to their identification as acetone 2,4-dinitrophenylhydrazone and methyl *n*-propyl ketone 2,4-dinitrophenylhydrazone, respectively. Despite its elementary analysis X-ray diffraction patterns indicated that the so-called C-4 fraction was predominantly the dinitrophenylhydrazone of methyl *n*-propyl ketone. The X-ray patterns are shown in Figure 4.

Distillation of the beany volatile material, as shown in Figure 5 and described in more detail later, gave a fraction (V-2) that would be expected to contain any high-boiling ketones. Preparation of the 2,4-dinitrophenylhydrazones of fraction V-2 gave a red powder which was chromatographed on silicic acid-

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[2] The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

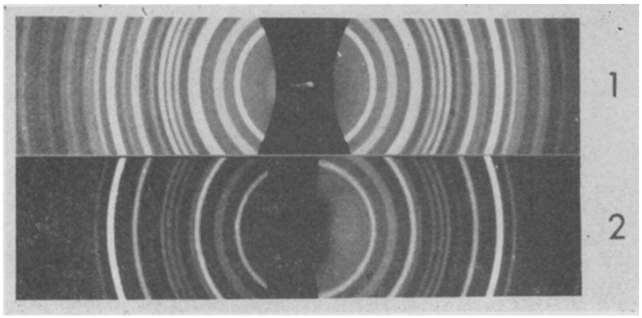

FIG. 4. X-ray diffraction patterns of 2,4-dinitrophenylhydrazones (1) acetone, (2) unknown C-3 carbonyl.

Celite to yield minor amounts of a strongly absorbed material and a predominant orange band.

Elution of this band and recrystallization of the product gave a substance having a melting point of 118°-120°C. This substance appears to be the 2,4-dinitrophenylhydrazone of an 11-carbon-atom carbonyl compound.

> *Anal.* calcd. for $C_{17}H_{24}N_4O_4$: N, 16.08. Found: N, 16.05.

The substance gave a negative test for dicarbonyl compounds. Maximum absorption in the ultraviolet occurred at 374 mμ., which is characteristic of 2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyls (9). It is of interest to note that the dinitrophenylhydrazone of methyl *n*-nonyl ketone is reported (1) to melt at 63°C. Insufficient material was available to permit further investigation of this carbonyl compound.

Silver-mirror tests of a number of carbonyl-containing fractions, obtained during the work described herein, were negative. This indicates that none of the carbonyl substances present in the beany-odor material is an aldehyde.

Distillation of the Beany Volatile Fraction

In a typical experiment 6.3 g. of beany volatile material were distilled as shown in Figure 5 to yield a low-boiling fraction (V-1) that collected in the dry-ice trap and also a higher boiling fraction (V-2). The beany-odor materials were carried over into the distillate while the residue contained higher fatty acids and their esters.

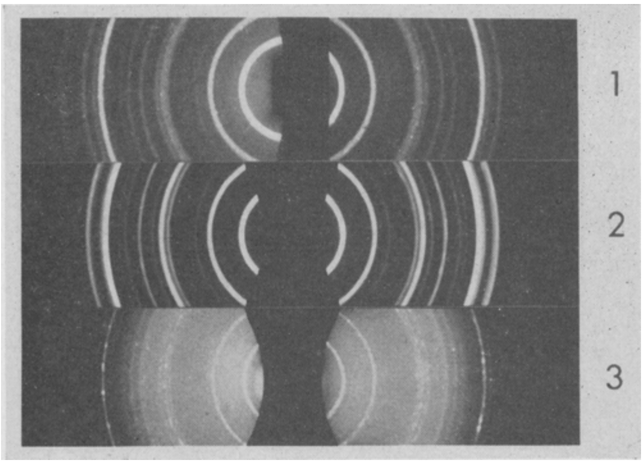

FIG. 4a. X-ray diffraction patterns of 2,4-dinitrophenylhydrazones (1) unknown C-2 carbonyl, (2) methyl *n*-propyl ketone, (3) unknown C-5 carbonyl.

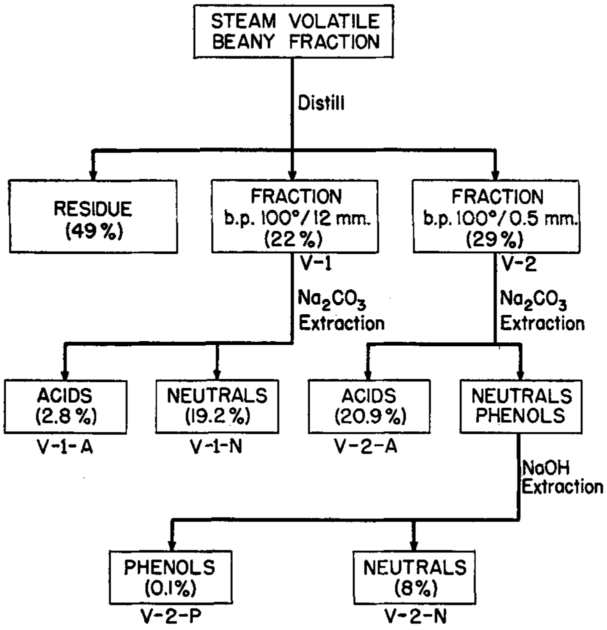

FIG. 5. Fractionation of steam-volatile beany material.

Acids. Fraction V-2 was diluted with ethyl ether and extracted with 5% aqueous sodium carbonate. Acidification of the alkaline solution yielded a layer of acidic material smelling strongly of caproic acid. An attempt to resolve this mixture of acids by paper chromatography according to the method of Kennedy and Barker (5) was only partially effective since only caproic acid could be clearly demonstrated to be present. However resolution by chromatography on silicic acid, using the method of Ramsey and Patterson (8), was very successful. A series of fractions was taken as the bands emerged from the column. Titration with sodium ethoxide gave a curve. Figure 6 shows the curve obtained with a known mixture of n-aliphatic acids. The sharp rise in the titration curve or the visible emergence of the band was taken as the threshold volume.

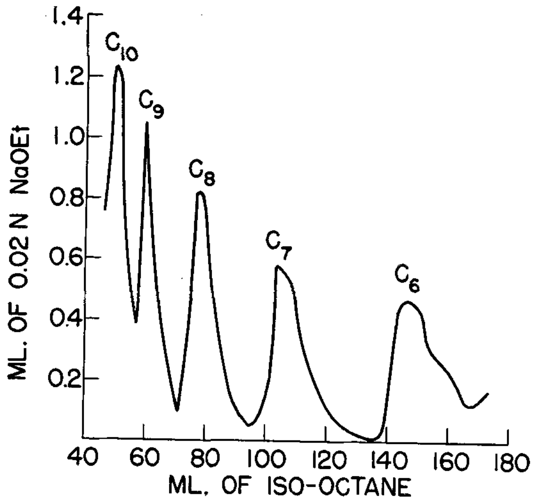

FIG. 6. Chromatography of *n*-fatty acids C-6 to C-10 on silicic acid.

This volume was characteristic of a given acid and may be used as a tentative identification. Whenever possible, known acids are added to an unknown and a single band confirms the identity of the unknown. When this procedure is not feasible, known mixtures are made up corresponding to the unknown, and the threshold volumes are compared. As an example, when fraction V-2-A was chromatographed, the threshold volumes obtained indicated the following acids: C-9, trace; C-8, 7.1%; C-7, 6.5%; C-6, 76.6%; C-5, 7.1%; and C-3, 2% (see Figure 7). Addition of C-8 and C-5 acids to the unknown gave a titration curve as shown in Figure 8, demonstrating that the unknown C-5 and C-8 acid bands are reinforced by the addition of known samples of these acids. Chromatographic examination of the acids in fraction V-1-A again showed a predominance of C-6 acid (87%) with a smaller amount (13%) of C-7 acid.

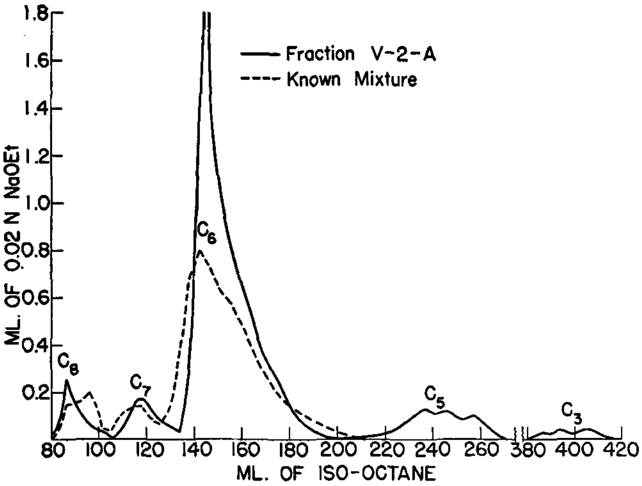

FIG. 7. Chromatography of acids in fraction V-2-A.

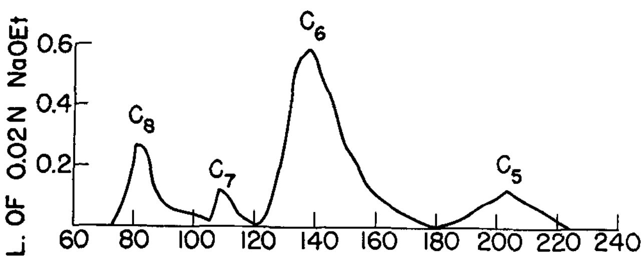

FIG. 8. Chromatography of acids in fraction V-2-A with added C-5 and C-8 acids.

Phenols. Extraction of the neutral material from fraction V-2 with 5% aqueous sodium hydroxide followed by acidification of this aqueous layer produced a dark oil with a strong phenolic odor. This material gave a brown-red coloration with ferric chloride and coupled to some extent with *p*-methoxybenzene diazonium salt as shown by the development of an orange-brown color. The phthalic anhydride-sulfuric acid test for phenols (11) was negative. Elementary analysis showed C, 66.41%; H, 8.79%; empirical formula, $C_{3.56}H_{5.67}O$. Ultraviolet spectroscopy demonstrated conclusively that this material contained phenolic substances. In Figure 9 absorption curves are shown for the unknown in cyclohexane and in aqueous alkali. The shift in the maximum from 2645 Å in cyclohexane to longer wave-lengths in aqueous alkali is characteristic of phenols. In order to obtain information on the complexity of the phenolic mixture, the sample was chromatographed on a 2 x 20-cm. column packed with silicic acid and developed with cyclohexane (13). Three-ml. fractions were taken and their absorption measured at 2645 Å. A plot of optical density *vs.* ml. of cyclohexane is shown in Figure 10. The sample appears to be a mixture of at least five materials.

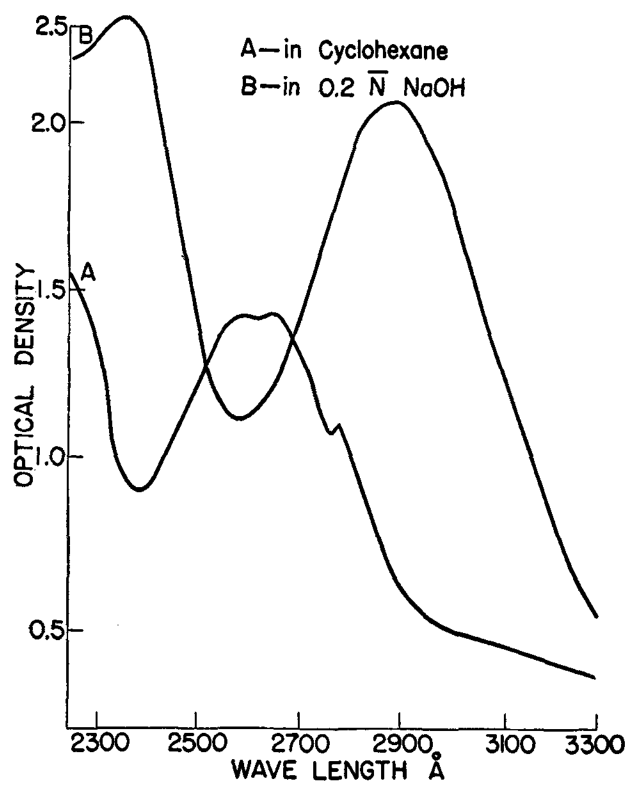

FIG. 9. Ultraviolet adsorption of phenolic fraction V-2-P.

Neutral Compounds. The neutral material (fraction V-2-N, Figure 5) remaining after extraction with sodium carbonate and sodium hydroxide was a yellow oil with a strong beany odor.

> Anal.: C, 71.29%; H, 10.48%; sap. value, 186; carbonyl oxygen, 3.5%; empirical formula, $C_{5.2}H_{9.2}O$.

Obviously the neutral fraction is a mixture containing esters, ketones, and possibly ethers and hydrocarbons. The carbonyl materials have been investigated (see *Carbonyl Compounds*), and a C-11 ketone is indicated. Distillation of the neutral oil in a small fractional distillation apparatus gave nine fractions, but carbonyl tests on all fractions indicate no resolution of the ketonic materials. The boiling range of the fractions (187°-226°C.) indicates ketones with 9 to 11 carbon atoms, which is in line with the information obtained on the 2,4-dinitrophenylhydrazones.

Saponification of the neutral oil (V-2-N) with ethylene glycol containing 0.5 N potassium hydroxide gave a neutral and an acidic material. The acidic material was chromatographed, using the methods of Ramsey and Patterson (8) and of Nijkamp (7) (de-

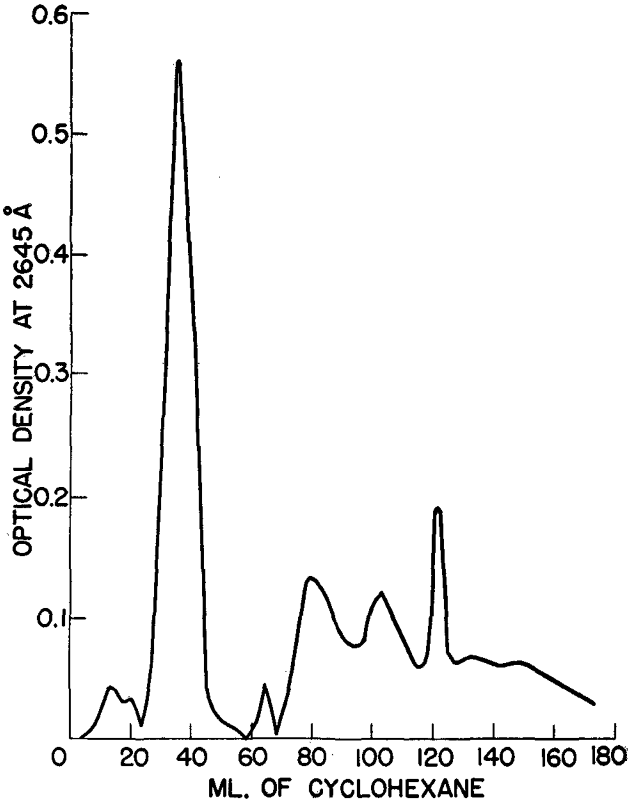

FIG. 10. Chromatography of phenolic fraction V-2-P on silicic acid.

scribed below in detail). The procedures of Ramsey and Patterson showed the following acids to be present (see Figure 11): C-10, 3.2%; C-9, 19.1%; C-8, 19.3%; C-7, 6.5%; and C-6, 1.9%. The remaining material was shown by Nijkamp's method to consist mainly of C-16 and C-18 acids. Distillation data on the neutral fraction suggest that these acids could be esterified with C_2 to C_6 alcohols. No information has been obtained on the alcoholic components of these esters.

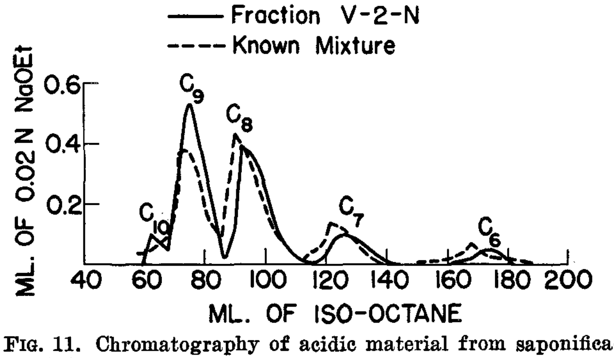

FIG. 11. Chromatography of acidic material from saponification of fraction V-2-N.

Investigations on the Green Oil Fraction

As indicated earlier, hydrolysis of the miscella during steam distillation could be responsible for many of the acidic materials found. It seemed desirable to attempt to extract the acidic materials before steam distillation. This was accomplished in part as shown in Figure 12. The miscella concentrate (660 g.) was diluted with 400 ml. of 47% alcohol and extracted with 250-ml. portions of petroleum ether until the hydrocarbon layer was colorless. Evaporation of the petroleum ether gave 48 g. (7.3%) of a green oil.

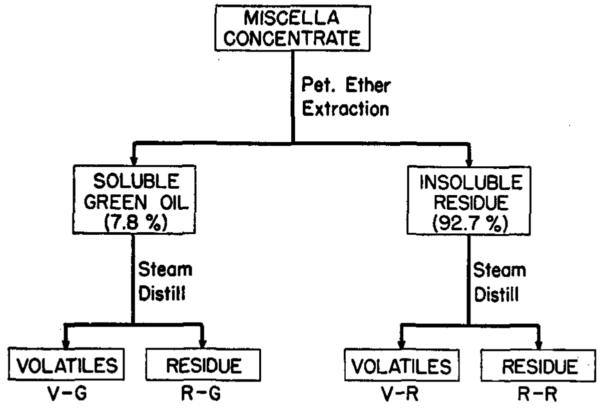

FIG. 12. Fractionation of miscella concentrate by extraction and steam distillation.

> Anal.: Iodine value, 80; sap. value, 198; carbonyl color reaction (6), positive; and acid value, 29.6.

Free Acids. Extraction of the green oil with 5% aqueous sodium carbonate gave a fraction containing higher fatty acids as well as lower ones. Since it seemed desirable to obtain some information on the type and amount of C-10 to C-20 acids, a chromatographic method suggested by Nijkamp (7) was used. In this procedure silicic acid powder (25 g.) was impregnated with methanol (20-25 ml.) containing bromothymol blue indicator (2 ml. of a 1% solution in methanol). The adsorbent was neutralized to the green color of the indicator with alcoholic ammonia and slurried with isooctane saturated with 90% methanol. The adsorbent was poured into a 2 x 20-cm. column and packed under a pressure of about 2 p.s.i. The separation of four saturated acids from each other is shown in Figure 13, which was obtained by application of the method to a synthetic mixture of equal weights of these acids. The peaks for oleic and linoleic acids show their positions when chromatographed alone. The presence of unsaturated fatty acids therefore would interfere with the separation of the saturated fatty acids. Application of this

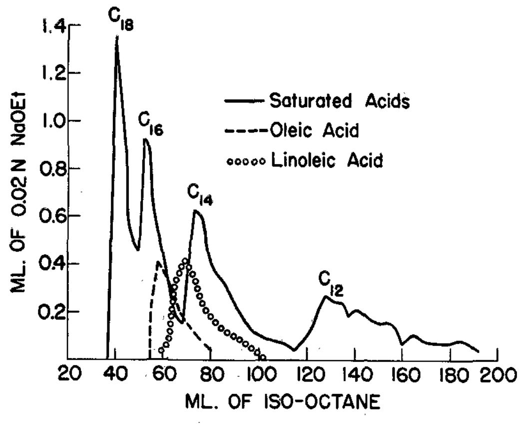

FIG. 13. Chromatography of n-fatty acids C-12 to C-18 on silicic acid.

method to the acids from the green oil showed the fraction to contain about 99% C-16 saturated and C-18 saturated, and unsaturated acids and caproic acid (1%).

On the basis of acid value the green oil contains 14.6% free acids or 0.14% caproic acid. This confirms the existence of caproic acid as a component in the original miscella concentrate.

Steam-Distilled Acids. Steam distillation of the green oil (40 g.) and extraction of the distillate (0.38 g.) with 5% sodium carbonate gave an acidic fraction (0.12 g.) containing caproic acid, 38.2%; C-7 acid, 20%; C-8 acid, 17.2%; C-9, 17%; and a C-10 acid, 7% (see Figure 14). From these data the amount of caproic acid (0.12%) obtained from the green oil by steam distillation is essentially the same as that obtained by extraction (0.14%). However the higher acids in the C-7 to C-10 range appear to be generated during steam distillation.

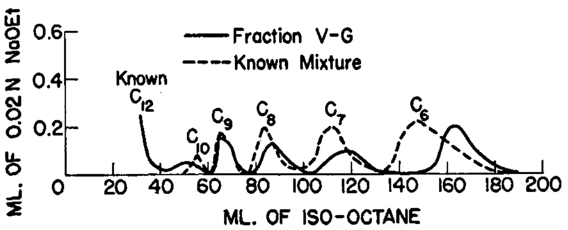

FIG. 14. Chromatography of steam-volatile acids from green oil, fraction V-G.

Steam distillation of the green-oil-free miscella and extraction of the distillate (V-R) with 5% sodium carbonate gave an acidic fraction (Figure 15) containing caproic acid, 69%; C-7 acid, 11%; and C-8 acid, 20%. The preponderance of caproic acid in the original miscella concentrate appears to come mainly from the fraction remaining after extraction of the green oil.

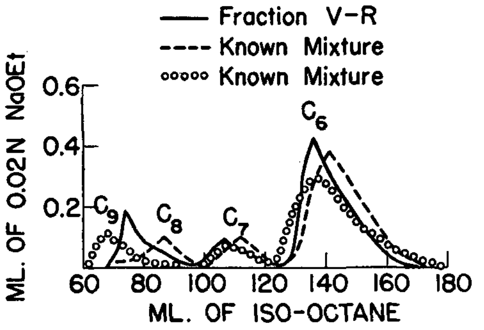

FIG. 15. Chromatography of steam-volatile acids from green-oil-free miscella, fraction V-R.

A possible explanation of the occurrence of the series of aliphatic acids isolated in this work is that they arise by oxidation of soybean oil, or unsaturated acids thereof, that may be present in the alcoholic extract. If this were the case, these acids should be found either free or, perhaps, as ethyl esters. In either case they should be extractable with petroleum ether. This explanation does not appear to be valid since only very small amounts of these acids could be extracted from the alcoholic miscella. It is concluded that these acids, in derivative form, are probably components of the odor bodies present in the original soybean flakes.

Summary

An alcoholic extract of hexane-extracted soybean flakes has been studied with the objective of isolation and identification of substances that might impart bitter or beany flavors to soybean flour. Bitter substances in this extract could be concentrated in a fraction soluble at low temperatures in ethanol or acetone. On partition of the bitter concentrate between water and organic solvents like hexane and ether, the bitter substances passed into the aqueous layer. Since no bitter material could be obtained by extraction of soybeans or soybean flakes with water, it appeared likely that the bitter substances in the extract were not identical with those in the original soybeans.

Beany-odor substances were obtained by steam distillation of the alcoholic extract. The beany material was found to contain ketones, carboxylic acids, esters, phenols, and some additional neutral components not identified (perhaps ethers or hydrocarbons). Acetone and methyl *n*-propyl ketone were isolated from the ketonic material and identified. An 11 carbon atom, α,β-unsaturated ketone was also isolated as its 2,4-dinitrophenylhydrazone. Its structure was not established further.

The free carboxylic acids identified by chromatography in the beany material consisted of caproic acid (about 77% by weight) with smaller amounts of acids having 3, 5, 7, 8, and 9 carbon atoms. Chromatography of the phenolic fraction indicated that it might be a mixture of at least five substances, but the small amount of material available precluded isolation and identification of these components.

Saponification of the ester fraction gave a neutral fraction that has not been further investigated and an acidic fraction. Chromatography of the acidic fraction showed that about 50% of this material consisted of unidentified acidic components and that the remaining 50% consisted of aliphatic carboxylic acdis having 6, 7, 8, 9, and 10 carbon atoms. The 8- and 9-carbon-atom acids were present in about equal proportion and accounted for 77% of the carboxylic acid fraction.

Extraction of the alcoholic extract with petroleum ether gave an oily material. Extraction of this oil with sodium carbonate gave an acidic fraction that was shown to consist mainly of 16- and 18-carbon-atom acids with only a trace of caproic acid. Steam distillation of the oily material yielded a small amount of acidic material containing 6-, 7-, 8-, 9-, and 10-carbon-atom acids. Steam distillation of the residue from which the oil had been extracted yielded a larger quantity of acids having 6, 7, and 8 carbon atoms. The lower aliphatic carboxylic acids thus do not appear to occur as free acids in the alcoholic extract but rather as derivatives that are only slightly soluble in petroleum ether but are hydrolyzable with steam. These results indicate that these carboxylic acids do not result from oxidation of unsaturated acids from soybean oil and that they are probably components of the actual odor bodies originally present in soybean flakes.

Acknowledgment

The authors wish to express their appreciation to N. N. Hellman and H. P. Zobel for the preparation and interpretation of X-ray diffraction patterns, to E. H. Melvin and B. L. Wilson for ultraviolet absorption spectra, and to C. H. Van Etten and C. E. McGrew for microanalyses.

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[Received December 22, 1954]

Acetone as a Selective Solvent for Vegetable Oils[1, 2]

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THE MODIFICATION of drying and semi-drying oils by extraction with a selective solvent has received considerable attention in recent years. A wide range of solvents has been investigated (9), but only furfural (2, 4) and liquid propane (1, 6) have warranted development to the point of commercial application. A third solvent which may find application in this field is acetone containing small proportions of water. Such a system was suggested by Jenkins (3) in a patent dealing with the use of "wet" furfural. It is a solvent which is readily available, is easily stripped from the oil, and requires no special equipment for handling. It has the added advantage that by varying the water content it may be "tailored" to the particular oil and separation involved.

Solubility and Selectivity

From the viewpoint of extraction efficiency the important properties of a solvent are a) solubility of the oil in it and b) selectivity, that is, the difference in iodine value between extract and raffinate on batch extraction. The effect of water content of acetone on these two properties is shown in Figures 1 and 2 for the batch extraction of a sample of soybean oil, I.V. 129.3, and a sample of linseed oil, I. V. 188.0. Solubility has been shown as the ratio of solvent to oil as this form is to be used later. Since a low solvent to oil ratio and high selectivity are desired, the variations of these properties with water content are conflicting. With reference to existing processes it appears however that a useful compromise can be obtained in the range of 3 to 7 parts water per 100 parts acetone by volume.

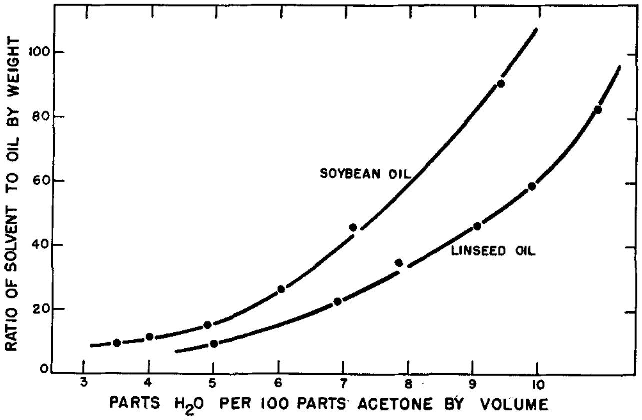

FIG. 1. Effect of water content of acetone on ratio of solvent to oil required at 25°C.

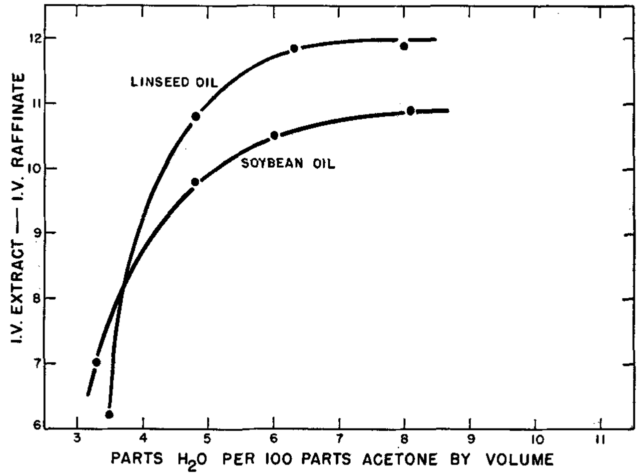

FIG. 2. Effect of water content of acetone on selectivity, *i.e.*, difference in iodine value between extract and raffinate oils.

Equilibrium Diagrams

The evaluation of the solvent for use in countercurrent column operation rather than in batch extraction is the important consideration. As in distillation the prediction and evaluation of extraction column operation is based on equilibrium data between phases over the concentration range involved. The particular type of equilibrium diagram used here is one adapted to extraction calculations by Maloney and Schubert (5) in which the ratio of solvent to solute is plotted against the concentration of components in the solute. As pointed out by Pratt (7) and illustrated by Rushton (8), in dealing with multi-component systems it is necessary to replace concentration by the value of some additive property of the system. The obvious choice of property in this system is iodine value. The required data are the solvent to oil ratios and iodine values of the oils in extract and raffinate phases over the range of iodine values likely to be encountered in fractionation. Ruthruff and Wilcock (9) in their

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[1] Presented at fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.

[2] Issued as Paper No. 190 on the "Uses of Plant Products" and as N.R.C. No. 3627.