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A Study of the Flavor Stability and Autoxidation of Beef Fats[1,2]

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BLAND FATS of high titer and low iodine value and of good flavor stability have always been in demand for the production of shortening and margarine. As beef tallow has a high melting point and a low iodine value, it could serve as a major source of hard fat for the compounding of shortenings. However beef tallow is subject to off-flavor and odor development and large price fluctuations which have placed it in an economically disadvantageous position (1). It would seem that the production of beef fats of higher flavor stability may help to solve the unstable price structure and help to increase their use in shortening, margarine, and other products. In the present study an attempt was made to characterize the compounds which cause off-flavors in edible tallow, to determine whether oxidative polymers are formed during the rendering process, and to determine whether beef tallow of better flavor stability could be produced.

Experimental

Isolation of Volatile Components Which Impart Characteristic Flavors and Odors to Edible Tallow. Fifteen hundred g. of edible tallow[4] were deodorized in an all-glass apparatus similar to one described by Bailey and Feuge (2), except that carbon tetrachloride was used instead of steam as the inert gas phase. The tallow was kept at 60°C. under a vacuum of 50 microns to minimize autoxidation and to avoid the development of odoriferous compounds during the process of deodorization. The rate of evaporation of carbon tetrachloride was controlled by proper cooling of the reservoir with an ice water bath. After about 10 ml. of carbon tetrachloride had evaporated, the apparatus was allowed to come to atmospheric pressure, the first cold finger of the trap was disconnected, the solid carbon dioxide and acetone cooling mixture were poured out, and the cold finger was suspended above a 25-ml. beaker. Warm water was poured into the cold finger, and the adherent material which had formed on the surface was allowed to melt and drip into the beaker. The solution was dried with anhydrous sodium sulfate.

Isolation of Volatile Components Which Caused Off-Flavors and Odors in Deodorized Edible Tallow. Three kg. of edible tallow were bleached with 3% by weight of official bleaching earth[5] and then deodorized in the all-glass apparatus at 75 micron pressure and 200°C. for 3 hrs. The deodorized product, which was bland in odor and flavor, was autoxidized at 60°C. in a 5-l., three-necked round bottom flask. This flask was fitted with a Tru-bore glass stirrer, a thermometer and a fritted glass tipped inlet, and an outlet aeration tube. Filtered air was introduced through the fritted glass tipped tube suspended in one neck of the flask. The effluent gas was passed through two cold traps, which were cooled with solid carbon dioxide and acetone, and the condensate was collected after 72 hrs. of autoxidation.

Solvent Extraction of Beef Fats. Approximately 2 kg. each of kidney, cod, caul and ruffle, and cold cutting fat of beef were extracted separately with Skellysolve F. The fats were trimmed, cut into cubes of about 2 cm.^{2}, and washed under cold running water. Although the trimming and the washing were done carefully, the fats were still contaminated with very small amounts of meat tissues and blood. The complete removal of the capillaries which ran into the fat seemed impossible. The washed cubes of beef fat were dried on blotting paper for 10 min., mixed with 1 kg. of anhydrous sodium sulfate, and ground twice through a 3/8-in. plate and once through a 1/8-in. plate in a meat grinder. The dough-like mixture was extracted with 10 liters of redistilled Skellysolve F until free of fatty materials. The extract was first washed with 400 ml. of ethyl alcohol and then washed six times with equal volumes of distilled water. The washed extract was dried with anhydrous sodium sulfate, and the solvent was removed under vacuum at 60°C. All the extraction processes were carried out under an atmosphere of nitrogen.

Organoleptic Evaluations of Beef Fats. The organoleptic tests were conducted in a manner similar to the one designed by Moser *et al.* (3). The samples to be tested were kept in 42 x 50 mm. weighing bottles fitted with ground glass covers, warmed to 50°C. in an aluminum block, and submitted to a panel of four individuals of long organoleptic testing experience. The aging of the samples was done in 600-ml. beakers. Three hundred ml. of the sample to be tested were transferred into the beaker, covered with a watch glass, and aged either at 60°C. for 6 days or 140°C. for 4 hrs.

Autoxidation of Oleo Oil. Seven hundred ml. of oleo oil were transferred to a 50 x 460 mm. glass tube, and the tube was suspended in a constant temptrature bath kept at 45 ± 0.5°C. Filtered dry air for aerating the oil was introduced through a fritted glass disk sealed into the bottom of the tube. The effluent air was passed through two glass traps connected in series and through a bubble counter. The traps were immersed in acetone and cooled with solid carbon dioxide. The

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[4] Obtained through courtesy of Swift and Company.
[5] The American Oil Chemists' Society, Chicago, Ill.

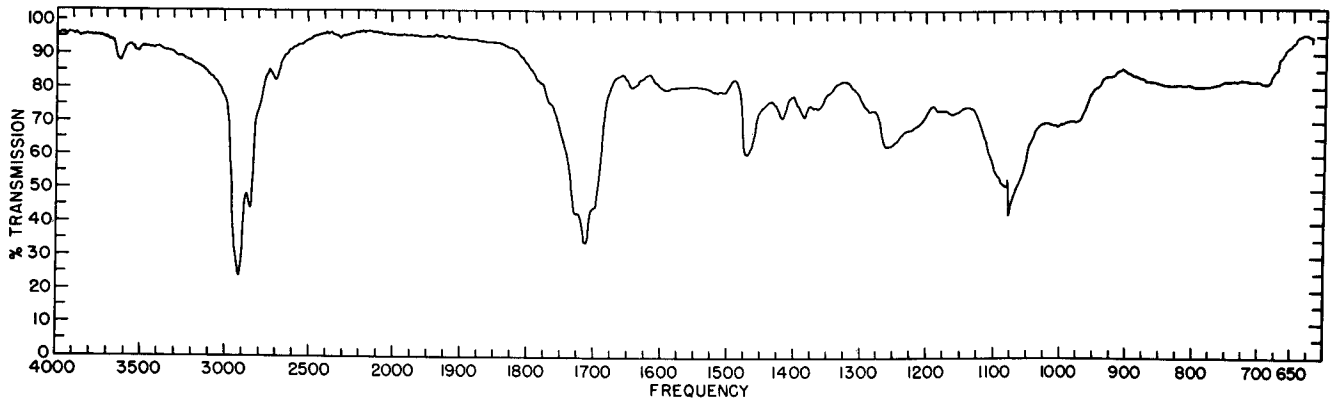

FIG. 1. The infrared absorption spectrum of the volatile components removed from undeodorized tallow by deodorization with carbon tetrachloride.

volatile components which condensed in the cold traps were washed out quantitatively every 24 hrs. with 5 ml. of carbonyl-free methyl alcohol. One ml. of the solution was used for a Lappin Clark test (4) to determine the amount of carbonyl compounds present. The color of the autoxidized oleo oil was determined every 24 hrs. by the spectrophotometric method as adopted by the American Oil Chemists' Society. Three ml. of oil were taken from the tube during suitable intervals for peroxide number determinations. Seven hundred ml. of soybean oil were autoxidized in exactly the same manner and in the same apparatus for comparison with oleo oil.

Catalytic Hydrogenation of Beef Fats. The selective hydrogenations of oleo oil and edible tallow were done under atmospheric pressure with either Raney nickel or Rufert nickel flakes as catalyst. Two kg. of the sample were transferred into a 5-l., three-necked round bottom flask, fitted with a Tru-bore stirrer, and heated to 90°C. under an atmosphere of nitrogen. The catalyst was then added, hydrogen was bubbled through the oil, and the effluent gas was led by a long piece of glass tube into open air. The temperature was raised to 110°C. in 10 min. and held at that temperature for either a half or one-and-a-half hours as desired. The hydrogenated products were deodorized with steam in an all-glass apparatus at 210°C. under a vacuum of 75 microns for 4 hrs.

Results and Discussion

The volatile odoriferous components of fresh undeodorized edible tallow were quite different from those obtained by autoxidation of a bland deodorized tallow. The odoriferous compounds obtained from the undeodorized tallow must have been formed during rendering as tallow obtained by solvent extraction under nitrogen in the laboratory did not have this kind of odor. The odor of these volatile compounds could not be diminished by treatment with carbonyl reagents, such as sodium bisulfite or hydroxylamine. The infrared absorption spectrum of a carbon tetrachloride solution which contained these compounds (Figure 1) indicated the possible presence of hydroxyl and carbonyl groups, aliphatic ether, ester, conjugation, carbon to nitrogen bonding, and a six-member lactone ring. The complexity of these volatile odoriferous compounds is clearly indicated.

If these odoriferous compounds are removed by deodorization, another type of odoriferous compounds may be formed on storage and cause "flavor reversion" in the tallow. In the present study these volatile compounds were obtained from deodorized tallow by autoxidation at 60°C. They had a painty to rancid odor and were carbonyl in nature as they could be removed by treatment with carbonyl reagents, such as sodium bisulfite or hydroxylamine.

Oleo oil, as manufactured by open kettle rendering at a temperature not exceeding 160°F. is composed of kidney, cod, caul and ruffle, and cold or cutting fat. In order to determine whether the components which were responsible for the undesirable odor and flavor originated from any particular fatty tissue and whether the precursors of those components were produced during the rendering process, a portion of a batch of each of the four different fatty tissues was processed in the laboratory by a solvent-extraction method under which oxidative polymers could not be formed. The stability of the products was then compared with that of oleo stock manufactured from the same batch of fats in the commercial plant.

Among the four beef tallows obtained by solvent-extraction of kidney, cod, caul and ruffle, and cold or cutting fat, the caul and ruffle fat had the highest color while the kidney fat had the least color. (Table I).

TABLE I

Chemical and Physical Constants of Beef Fats

Source	Fat	Melting Point (Wiley, °C.)	Iodine No. (Wijs)	Color (Photometric Method)
Solvent extracted in laboratory	Cod	43.5	46.05	1.43
	Caul and ruffle	47.5	40.80	4.57
	Cold or cutting	34.0	53.29	1.82
	Kidney	46.5	39.94	0.97
Rendered under nitrogen in laboratory	Cod	43.5	43.72	1.27
	Caul and ruffle	49.5	37.81	4.01
	Cold or cutting	41.0	50.51	1.43
	Kidney	44.0	42.79	0.40
Commercial product	Oleo stock	47.8	41.61	2.11

The caul and ruffle fat, which appeared as the softest of the four before extracting, yielded a product which had the highest melting point. The cold or cutting fat, which has often been called hard cutting fat, yielded a product which had the lowest melting point.

There were no significant differences in the composition of the highly unsaturated fatty acids among the four different beef fats (Table II). However both linolenic and arachidonic acids were present in higher concentrations in cold or cutting fats than in the other three fats. The amounts of conjugated fatty acids present were calculated from the absorptions shown in the ultraviolet region. The interference due to the pigment components in the beef fats was not corrected

TABLE II

Fatty Acid Composition of Beef Fats

Source	Fat	Saturated (%)	Oleic (%)	Conjugated (%)			Non-Conjugated (%)		
				Diene	Triene	Tetraene	Linoleic	Linolenic	Arachidonic
Solvent extracted in laboratory	Cod	50.57	40.36	0.55	0.00	0.00	3.80	0.29	0.02
	Caul and ruffle	55.77	34.89	1.13	0.03	0.00	3.31	0.43	0.04
	Cold or cutting	42.21	48.79	0.89	0.01	0.00	2.67	0.79	0.24
	Kidney	54.43	38.01	**0.37**	0.01	0.00	2.44	0.31	0.03
Rendered under N_2 in laboratory	Cod	50.38	42.33	0.53	0.01	0.00	1.93	0.38	0.04
	Caul and ruffle	57.04	35.63	0.94	0.03	0.00	1.53	0.37	0.06
	Cold or cutting	43.42	49.37	0.84	0.01	0.00	0.89	0.82	0.25
	Kidney	52.60	42.65	0.37	0.01	0.00	1.78	0.31	0.03
Commercial product	Oleo stock	52.70	40.17	0.65	0.01	0.00	1.56	0.42	0.09

for. It should be noted that the amount of conjugated fatty acids thus calculated is proportional to the color (photometric) of the respective fat.

The percentages of linoleic acid in the rendered fats were lower than in the corresponding solvent-extracted beef fats. This discrepancy may have been due to *cis-trans* isomerization which may occur during rendering. Swern, Knight, and Eddy (5) in their study of the *trans* octadecenoic acid content of beef fat also considered the possibility of *cis-trans* isomerization which may occur during commercial processing. However extraction with solvents would remove phospholipids more thoroughly than the wet rendering process. As phospholipids contain a larger percentage of linoleic acid than triglycerides, the linoleic acid content of extracted fats would be higher than that of the rendered fats.

The beef fats obtained by solvent extraction at room temperature under nitrogen had a slight solvent odor even though the solvent which was used for extraction was redistilled and the fat was freed from solvent under 2 mm. vacuum with agitation at 60°C. for 6 hrs. However the beef fats obtained by solvent extraction did not have the characteristic odors of oleo oil and of edible tallow. It was therefore concluded that these odors were developed during rendering.

After aging at 140°C. for 4 hrs., all four beef fats obtained by solvent extraction developed a musty tallowy odor and off-flavor (Table III). Organoleptic

TABLE III

Comparison of Flavor Stability of Solvent-Extracted and Heat-Rendered Beef Fats

Source	Fat	Score (Panel Testing) Aged at 140°C. for 4 Hours
Solvent extracted in laboratory	Cod	5.7
	Caul and ruffle	5.0
	Cold or cutting	5.6
	Kidney	5.4
Commercial product	Oleo stock	4.8
	Edible tallow	1.7

evaluations indicated that the beef fats obtained by solvent extractions were better than oleo stock or edible tallow obtained in the commercial plant from the same batch of fatty tissues. However the improvement was only comparative, and all the samples prepared by solvent extraction under conditions in which oxidative polymers could not be formed also developed off-flavor and odor after aging.

Oleo oil underwent considerably different changes from soybean oil when both were autoxidized under exactly the same conditions (Figure 2). The present results indicated that more carbonyl compounds were obtained from oleo oil than soybean oil from the second through the eighth day of oxidation. After that

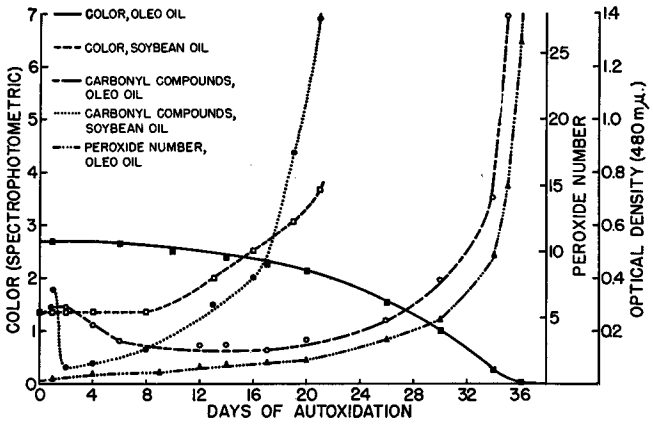

FIG. 2. Physical and chemical changes during autoxidation of oleo oil and soybean oil.

however the amounts of carbonyl compounds obtained from soybean oil rapidly increased while that obtained from oleo oil was up to the 20th day almost constant. At the end of 20 days of autoxidation the amount of carbonyl compounds obtained from oleo oil also increased rapidly and reached the same level as soybean oil at the 35th day. That more carbonyl compounds were obtained from soybean oil in the first day and from oleo oil in the first two days than were obtained in the next few days indicated that both oils contained a small amount of decomposition products which might have formed during processing, shipping, and storage. This may also explain the larger amount of carbonyl compounds obtained from oleo oil than from soybean oil during the first few days of autoxidation. The oleo oil was not deodorized and therefore may contain more volatile decomposition products formed during processing and storage. The carbonyl compounds formed by autoxidizing oleo oil seemed to be less volatile than those formed from soybean oil and took a longer time to be displaced from the oil by the current of nitrogen. It should be noted that both of the oils which were used in this experiment were obtained directly from processing plants and were stored under refrigeration before use.

The increase in peroxide number during the autoxidation of oleo oil almost paralleled the increase in the amount of carbonyl compounds collected. Since this correlation was expected, it seemed to indicate that the measurement of carbonyl compounds had the desired accuracy. The color of oleo oil decreased only slightly during the first 20 days and then bleached rapidly to colorless during the next 16 days. On the other hand, the color of soybean oil held constant for the first 8 days and then increased rapidly during the next 13 days to a brownish yellow color. This dark color of soybean oil could be bleached by further oxi-

dation. However, at that stage of autoxidation, considerable amounts of oxidative polymers were formed in the soybean oil (6).

It was interesting to note that during the autoxidation of oleo oil, the peroxide number as well as the formation of volatile carbonyl compounds increased rapidly as the color of the oil began to decrease. The decoloration of oleo oil also occurred during deodorization. The present results indicated that such decoloration is not entirely due to thermal effects. When oleo oil was sealed under various degrees of vacuum and heated to 180°C., the rate of decoloration of the oil was proportional to the amount of oxygen available (Table IV). Furthermore addition of antioxidants to the oleo oil decreased its tendency to decolorize.

TABLE IV

Effect of Autoxidation on the Thermal Decolorization of Oleo Oil

Sample	Heat Treatment		Color (Photometric Method)			
	Temperature (°C.)	Pressure (mm.)	0 Hour	1 Hour	2 Hours	5 Hours
Oleo oil	180	760	2.94	0.50	.....	.....
Oleo oil	180	1	2.94	.....	1.67	0.91
Oleo oil	180	0.1	2.94	.....	3.02	1.58
Oleo oil + 0.05% Tenox II	180	0.1	2.94	.....	.....	2.02

Oleo oil does not form oxidative polymers as readily as soybean oil. When the latter was autoxidized by air at 60°C. for 12 days, oxidative polymers separated out as an insoluble layer when the autoxidized product was mixed with pentane-hexane (6). On the other hand, when oleo oil was autoxidized in the same manner, no such separation could be accomplished (Table V). Even at the end of 36 days of autoxidation, the oxidized product yielded only a slight turbidity when dissolved in pentane-hexane, but no polymers separated.

When 1,500 g. of oleo oil were deodorized at 210°C. under 75 microns for 4 hours, 300 ml. of water were used to generate steam. This water could be recovered from the dry ice traps as a milky solution with a strong, unpleasant odor. This odor, unlike that obtained on the deodorization of soybean oil, could not be completely removed by carbonyl reagents, such as aqueous sodium bisulfite and hydroxylamine hydrochloride. But this unpleasant odor could readily be converted into a faint fruity odor by shaking with freshly prepared Raney nickel. Furthermore the water recovered from the cold traps after the deodorization of hydrogenated oleo oil did not have the same odor as that obtained after the deodorization of unhydrogenated oleo oil. This led to the belief that a very slight hydrogenation of high selectivity may remove the characteristic odors of oleo oil and edible tallow

TABLE V

Formation of Oxidative Polymers at 60°C.

Days Exposed to Air	Soybean Oil		Oleo Oil	
	Ref. Index (30°C.)	Solubility	Ref. Index (50°C.)	Solubility
0	1.4722	Soluble in pentane-hexane	1.4535	Soluble in pentane-hexane
12	1.4780	Oxidative polymers separated out as a layer from pentane-hexane	1.4541	Soluble in pentane-hexane
24	.....	.....	1.4556	Form slight turbidity with pentane-hexane
36	.....	.....	1.4566	Form slight turbidity with pentane-hexane

and improve their flavor stability. This was shown to be true by the present results.

Catalytic hydrogenation of oleo oil and edible tallow under conditions of high selectivity removed the characteristic odors and produced fats of high flavor stability (Tables VI and VII). This hydrogenation

TABLE VII

Improvement of Flavor Stability of Edible Tallow by Selective Hydrogenation with 0.3% of Ruffert Nickel Catalyst Under Atmospheric Pressure at 110°C.

Fat	Antioxidant Added	Characteristics of Fats			Score (Panel Testing) Aged at 140°C. for 4 Hours
		Melting Point (Wiley) °C.	Iodine No. (Wijs)	Refractive Index (50°C.)	
Edible tallow	None	47.7	44.2	1.4538	1.7
Hydrogenated edible tallow	None	49.5	42.9	1.4530	4.8
Hydrogenated edible tallow (deodorized)	None	49.5	42.9	1.4528	6.5
Hydrogenated edible tallow (deodorized)	0.05% Tenox II	49.5	42.9	1.4528	6.8
Shortening I[a]	.....	46.5	78.9	1.4569	5.5
Shortening II[a]	.....	50.2	66.7	1.4558	5.7

[a] Shortening I was made from hydrogenated vegetable oils. Shortening II was made from meat and vegetable fats.

under atmospheric pressure was so slight that the iodine number decreased by less than 4 and the melting point increased by less than 2°C. After deodorization the hydrogenated oleo oil and edible tallow were not only bland in odor and flavor but also had a flavor stability better than that of some of the best shortenings available on the market. By the use of the carbonyl index method (7) the improvement in flavor stability of oleo oil and edible tallow by this slight hydrogenation could be clearly shown (Table VIII). The mechanism involved in the removal of the characteristic odors of oleo oil and edible tallow by selective hydrogenation is difficult to ascertain. However the improvement of flavor stability seemed to parallel a

TABLE VI

Improvement of Flavor Stability of Oleo Oil by Selective Hydrogenation Under Atmospheric Pressure at 110°C.

Fat	Catalyst	Antioxidants Added	Characteristics of Fats			Score (Panel Testing) Aged at 140°C. for 4 Hours
			Melting Point (Wiley) °C.	Iodine No. (Wijs)	Refractive Index (50°C.)	
Oleo oil	.....	None	37.5–39.8[a]	45.1–46.3[a]	1.4539	3.7[b]
Oleo oil, hydrogenated for ½ hour	1% Raney Ni	0.05% Tenox II	38.0	44.1	1.4539	6.7
Oleo oil, hydrogenated for 1½ hours	1% Raney Ni	None	40.7	41.4	1.4531	6.4
Oleo oil, hydrogenated for 1½ hours	0.7% Rufert Ni	0.05% Tenox II	39.4	43.0	1.4531	6.7
Shortening I[c]	.....	.....	46.5	78.9	1.4569	4.6
Shortening II[c]	.....	.....	50.2	66.7	1.4558	5.7

[a] From three different samples. The sample used for hydrogenation had a melting point of 37.5°C. and an iodine number of 46.3.
[b] Varies with different samples.
[c] Shortening I was made from hydrogenated vegetable oils. Shortening II was made from meat and vegetable fats.

TABLE IX

Changes in Fatty Acid Composition of Edible Tallow and Oleo Oil by Selective Hydrogenation

Fat	Conditions of Hydrogenation				Fatty Acid Composition (%)					
	Catalyst	Temp. °C.	Pressure	Time (hr.)	Conj. Diene	Saturated	Oleic	Linoleic	Linolenic	Arachidonic
Oleo Oil	.....	.....	.....	.....	0.57	48.58	44.60	1.29	0.43	0.12
Hydrogenated Oleo Oil	1% Raney Ni	110	Atm.	1½	0.07	49.82	45.56	0.13	0.01	0.01
Edible Tallow	.....	.....	.....	.....	0.61	49.05	44.56	0.91	0.39	0.07
Hydrogenated Edible Tallow	0.3% Rufert Ni	110	Atm.	1½	0.02	48.91	45.88	0.64	0.15	0.00

TABLE VIII

Improvement of Flavor Stability of Oleo Oil by Selective Hydrogenation as Measured by the Carbonyl Index Method

Method of Aging	Oleo Oil	Deodorized Oleo Oil	Hydrogenated Oleo Oil
No aging	137	less than 10	less than 10
Aged at 60°C. for 6 days	157	103	82
Aged at 100°C. for 2 days	1,002	1,468	239

decrease in the arachidonic and linolenic acid content of the oleo oil and edible tallow on hydrogenation (Table IX).

Summary

The odoriferous compounds isolated from a fresh edible tallow were found to be very complex in nature and could not be diminished by treatment with carbonyl reagents. When these compounds were removed by deodorization, the bland tallow which was obtained developed on autoxidation another type of odoriferous compounds. The latter contained various carbonyl compounds of the type which have been associated with flavor reversion in edible oils.

The characteristic odor of oleo oil and edible tallow could be removed by slight hydrogenation of high selectivity under atmospheric pressure. This hydrogenation process raised the melting point by less than 2°C. but substantially decreased the linolenic and arachidonic acid content. The hydrogenated products, after deodorization, were not only bland in odor and flavor but also had flavor stabilities better than those of some of the best commercial shortenings.

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Some Preliminary Investigations Directed Toward Increasing the Utility of Cottonseed Soapstock[1]

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BY-PRODUCT SOAPSTOCK that results from the refining of cottonseed oil contains numerous diverse substances. With some exceptions all the minor constituents of crude cottonseed oil (3), phosphatides, sterols, inositol esters, resins, carbohydrates, proteins, and pigments, to list a few, may be expected, in enhanced amounts, in soapstock. Keith *et al.* (4) compiled from the literature a list of minor constituents and the range, percentage-wise, of their occurrence in crude oil. Many of these constituents are, at the very least, interesting to the chemist; some are undoubtedly valuable. However the fact that the major constituents (water, fatty acid soaps, and neutral oil) of soapstock amount to well over 80% by weight of the total, makes recovery of the minor components individually or severally a difficult economic operation. Further, unmarketed soapstock constitutes a disposal problem, and any plan designed to recover some minor component needs careful examination lest the disposal problem be intensified. The foregoing considerations, in effect, restrict investigations directed toward an increased utility for soapstock to the major constituents.

Benzylation

Gomberg and Buchler (2) reported preparation of the benzyl esters of fatty acids by reacting sodium soaps and benzyl chloride. Fair yields were obtained both in the presence and the absence of water. For adaptation of this type of reaction to soapstock, removal of water was the first step. Dehydration accomplished two purposes. First, it effectively reduced the amount of material handled. Second, residual alkali in the raw soapstock effected some reduction in unsaponified neutral oil during the dehydration. It should be noted that benzyl chloride, although not unduly reactive with water alone, by virtue of a limited solubility reacts violently with certain other materials, notably iron, so that glass or enameled ware should be used for carrying out the benzylation reactions.

Dehydration of the soapstock was accomplished by azeotropic distillation of the water, using a trap that permitted rejection of the water while the other member of the azeotrope was returned to the reaction flask. As an added advantage, this method of drying left the dehydrated soapstock well dispersed and suspended in a liquid medium that served in the next operation as the reaction medium for the dry soaps and the benzyl chloride. The liquid selected for the dual role of dehydration and reaction medium must be reasonably inert, immiscible with water, and possess a suitable boiling range. Aromatic solvents, toluene, xylene, cumene, and cymene, were successfully employed, although they gave rise to severe foaming of the soaps during the final stages of dehydration. After dehydration the dry soapstock still

[1] Presented at 46th annual meeting, American Oil Chemists' Society, New Orleans, La., April 18–20, 1955.
[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.