TABLE II

	Soap	A	B	C	D	E
pH of 1% solution	8.7	8.0	8.0	7.5	8.2	7.8
Foam power in moderate hard water, rated 0–10	10	4	3	7	9	8
Foam power in water of 600 p.p.m. as $CaCO_3$	....	4	3	5	7	5
Texture under use test	Good	Poor	Bad	Good	Good	Fair
Feel of bar after soaking and air drying	Slimy	Slimy	Firm	Firm	Slimy	Slightly slimy
Sloughing effect under conditions yielding a 10% loss to soap	10%	35%	5%	4%	11%	14%

characteristics of soap, that is, it must not slough away when left wet, must have a smooth texture, must not crack, must foam well, and have good detergency without skin defatting (3). In addition, the synthetic bar must not leave a bathtub ring, must foam and have good detergency in the hardest water, and should take advantage of a low pH value. How well these ideals have been approached may be noted from the following tabulation, Table II, based on a few typical examples of commercial and experimental formulations. Soap is used as a basis for comparison.

An examination of the above table indicates that D most closely resembles soap, with E a close second. Both represent satisfactory synthetic bar formulations when consideration is given to their superior foam power in hard water and to their low pH values as compared to soap. Example C however, except for slightly inferior foam power, greatly excels soap in its resistance to wasting away, its feel under semi-dry conditions, and its low pH value which approaches that of a normal skin. This type of formulation would be very satisfactory. Formulations A and B would be unsatisfactory on foam value, and A in particular on its tendency to slough away.

It thus appears that synthetic bars of excellent quality can be made from presently available raw materials that are superior to soap except in perhaps a few minor details and that their impact on the 250,000-ton-a-year market is at present being felt in the trade. It is the author's opinion that the future will see a great shift in this market from soaps to detergents although the effect of this change will not be as devastating on the tallow market as that produced by detergent powders. This view is based on the part soap and tallow derivatives may play in the future formulation of such products.

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N-Bromosuccinimide in the Conjugation of Fatty Acids and Oils

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CREATION of new conjugated double bonds for improving the drying properties of fatty oils or acids of low unsaturation has been frequently reported. This may be brought about through chlorination, followed by dehydrochlorination (1), dehydration of hydroxylated fatty oils (2, 3), or introduction of hydroxyl groups by oxidation accompanied by dehydration (4).

Methods for effecting conjugation by the isomerism of polyunsaturated fatty acids are well known (5, 6). Brode *et al.* (7) have shown that debromination of tetrabromo derivative of 9:12-linoleic acid produces to some extent conjugated unsaturated acids. Recently Teeter *et al.* (8) reacted *tert*-butyl hypochlorite with methyl oleate, methyl linoleate, and some vegetable oils under various conditions and then by thermal dehydrochlorination introduced conjugation, principally of diene and triene type. In the case of methyl oleate they found that the products consisted mostly of a mixture of allylic and nonallylic monochloro derivatives and a saturated dichloro derivative, possibly methyl 9,10-dichlorostearate. Methyl linoleate was converted by *tert*-butyl hypochlorite and methanol to methyl dimethoxy dichlorostearate; its thermal decomposition resulted in the formation of a 21.7% methyl diketostearate. Teeter *et al.* explained these reactions by a free-radical chain process. More recently Arnold (9) has obtained a patent on the use of alkali metal hypochlorite for the same purpose.

Ziegler *et al.* (10) have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced with bromine by means of N-bromosuccinimide. By this reaction Teeter (8) introduced bromine in the allylic position in methyl esters of soybean fatty acids and methyl linoleate. Schmid and Lehmann (12) brominated methyl elaidate and methyl brassidate with N-bromosuccinimide and, after dehydrobromination, isolated 9:11-octadecadienoic and 13:15-docosadienoic acids. Gunstone (13) has however pointed out that the properties of the

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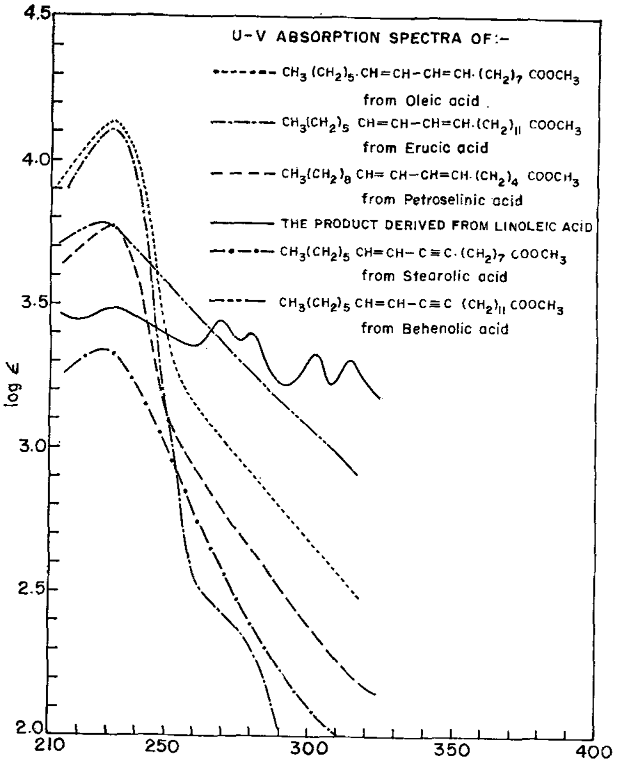

FIG. 1.

former acid differ from those of the known *trans-trans* 9:11-octadecadienoic acid and that confirmation of these results is desirable. Sutton and Dutta (14) observed that both the 8- and 11-monobromo-oleates together with a small quantity of the dibromo-ester were formed when methyl oleate was reacted with an equivalent amount of N-bromosuccinimide. They however could not separate the two mono-bromo isomers in a pure state. In agreement with Schmid and Lehmann (12) and Clemo and Stevens (15) we also infer from our studies on the ozonolysis of the dehydrobrominated products that bromination generally occurs on the allylic CH_2 group distant from the carboxylic group.

Bergstrom and Hansson (16) reacted methyl linoleate with N-bromosuccinimide in ultraviolet light and reported the formation of diene during bromination as a result of the tautomerism of the double bond system in a free-radical reaction.

Previously we reported (17) that the allylic bromination of the methyl esters of oleic, petroselinic, erucic, stearolic, and behenolic acids with N-bromosuccinimide, followed by thermal dehydrobromination, gave the corresponding conjugated fatty acids in yields of 30–40%. The work has now been extended to 9:12-linoleic acid and also to some seed oils [mustard, peaunt, safflower, *Pangomia glabra* (karanja), *Azadirachta indica* (neem), olive, tobacco oils].

TABLE I
Characteristics of Methyl Esters and of the Products Resulting from Allylic Bromination Followed by Thermal Dehydrobromination

Methyl ester of fatty acid	Original		After reaction with N-bromosuccinimide and dehydrobromination		
	Iodine value [a]	$n^{50°}/D$	Iodine value [a]	$n^{50°}/D$	Diene value [b]
Erucic	74.5	1.4475	96.0	1.4690	38.4
Oleic	89.8	1.4420	128.0	1.4640	42.8
Petroselinic	89.9	1.4421	121.4	1.4682	39.7
Stearolic	85.1	1.4452	123.4	1.4772	36.2
Behenolic	70.5	1.4582	109.3	1.4722	37.3
Linoleic	180.4	1.4530	247.3	1.4725	67.5

[a] Iodine value determinations were carried out by the Rosenmund-Kuhnhenn method as modified by Planck, Pack, and Goldblatt (22).

[b] The diene value is expressed in terms of the equivalent number of centigrams of iodine per gram of the sample (23).

Experimental

All fatty acids and oils were of high-grade purity. The fatty acids were converted to their methyl esters as usual. The experimental details of the bromination of methyl oleate and peanut oil with N-bromosuccinimide and their subsequent dehydrobromination are given below. Similar treatment is applicable to other esters and oils.

Bromination of Methyl Oleate with Equimolecular Proportion of N-Bromosuccinimide. A 500-ml., three necked flask, equipped with a mercury-sealed stirrer, a condenser with $CaCl_2$ tube, and an inlet for dry nitrogen gas was employed. To a solution of methyl oleate (30 g., 0.1 mole) in carbon tetrachloride (150 ml.) was added N-bromosuccinimide (18 g., 0.1 mole) and benzoyl peroxide (0.6 g.). The reaction mixture under nitrogen atmosphere was stirred and heated gradually to 70°. After the exothermic reaction subsided, refluxing was continued for 1½ hr. Filtration of the mixture removed succinimide and unreacted N-bromosuccinimide from an orange solution of brominated methyl oleate.

Thermal Dehydrobromination of Methyl Bromo-Oleate. The above orange solution of methyl bromo-oleate was transferred to another 500 ml., two-necked flask, fitted with a condenser and a $CaCl_2$-tube, and was heated on a water bath under a continuous current of nitrogen until a test with ammonia indicated that no more hydrogen bromide was being evolved.

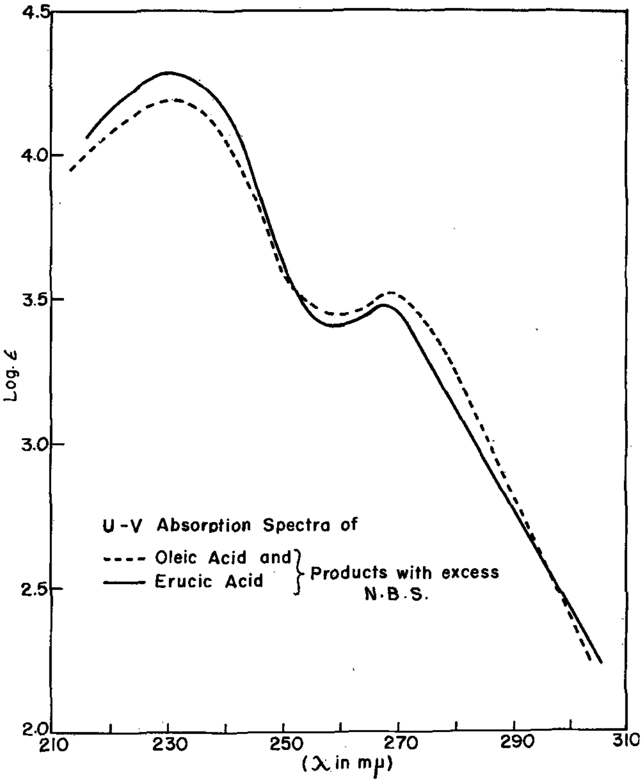

FIG. 2.

The solvent was removed under vacuum. The viscous product was dissolved in petroleum ether (b.p. 40–60°) and chromatographed over silica gel, using ethyl ether as eluant. Characteristics and the ultraviolet absorption spectrum of the major halogen-free fraction (11.2 g.) are given in Table I and Figure 1, respectively.

Similar data of the products obtained from methyl esters of petroselinic, erucic, stearolic, and behenolic acids are recorded in Table I and Figure 1.

Treatment of Methyl Oleate with Excess of N-Bromosuccinimide and Subsequent Thermal Dehydrobromination. A mixture of methyl oleate (30 g., 0.1 mole), N-bromosuccinimide (60 g., 0.3–0.4 mole) and benzoyl peroxide (1 g.) in carbon tetrachloride (200 ml.) was refluxed under nitrogen for 2 hr. at 80–85°. The orange solution was then subjected to thermal dehydrobromination. The resultant product (10 g.) after chromatographic purification was found to contain no halogen. Its ultraviolet absorption curve as well as that of the material obtained from methyl erucate are shown in Figure 2.

Ozonolysis of the Dehydrobrominated Product from Methyl Oleate. Ozonized oxygen was passed into a solution of dehydrobrominated product from methyl oleate (20 g.) in anhydrous ethyl acetate (250 ml.) at 0° for 20 hr. The solvent was removed at about 30° by a stream of dry air. The ozonide was decomposed in water at 60–70°. The mixture was steam-distilled. The product was extracted from the distillate with ethyl ether, dried over anhydrous sodium sulphate, and recovered as usual. The product distilled at 125–128°/4 mm. weighed 4.1 g. Anal. found: C, 64.3%; H, 10.5%; Neut. equiv. 130. Calc. for $C_7H_{14}O_2$: C, 64.6%; H, 10.8%; Neut. equiv. 130. The amide was prepared in the usual manner. Its melting point and mixed m.p. with an authentic specimen of heptylic amide was 92–94°.

Ozonolysis of Dehydrobrominated Product from Methyl Petroselinate. A solution of the dehydrobrominated product from methyl petroselinate (5 g.) in anhydrous ethyl acetate (80 ml.) was ozonized at 0°. The ozonide was decomposed with hydrogen peroxide. The steam-volatile product was recovered as above. It distilled at 135°/3–5 mm. (bath-temp.). Yield: 1.1 g. Anal. found: C, 69.6%; H, 11.4%; Neut. equiv. 170. Calc. for $C_{10}H_{20}O_2$: C, 69.8%; H, 11.6%; Neut. equiv. 172.

Bromination of Peanut Oil with N-Bromosuccinimide. A mixture of peanut oil (25 g.), N-bromosuccinimide (20 g.), and benzoyl peroxide (0.6 g.) in carbon tetrachloride (175 ml.) was refluxed for 1½ hr. The reaction product was cooled and filtered.

Dehydrobromination of the Brominated Peanut Oil with 2:4:6-Collidine. This solution was mixed with 2:4:6-collidine (125 ml.) and refluxed for 1 hr. The collidine hydrobromide was filtered off, and the filtrate was concentrated in a water-bath under reduced pressure. The syrupy residue was taken up in ethyl ether, treated with dilute hydrochloric acid (1:1), and washed several times successively with water, sodium carbonate solution (1%), and water. It was dried over anhydrous sodium sulphate. Removal of the solvent *in vacuo* gave a dark brown thick liquid. The iodine and diene values of the material are recorded in Table II. A small sample was dissolved in petroleum ether (b.p. 40–60°) and chromatographed over silica gel with ethyl ether as the eluant. The chromatographed sample was examined for its characteristics and ultraviolet absorption spectrum (Figure 3). Similar data for the other oils are also recorded in Table II and Figure 3.

TABLE II

Characteristics of Various Unsaturated Oils and of the Products Resulting from Allylic Bromination Followed by Dehydrobromination

Vegetable oils	Original		After reaction with N-bromosuccinimide and dehydrobromination		
	Iodine value[a]	$n^{60°}/D$	Iodine value[a]	$n^{60°}/D$	Diene value[b]
Mustard	96.0	1.4614	115.5	1.4800	21.9
Peanut	93.2	1.4592	118.2	1.4850	33.0
Olive	83.6	1.4590	106.3	1.4643	23.7
Tobacco seed	138.6	1.4651	150.9	1.4880	26.3
Safflower seed	139.6	1.4622	146.3	1.4873	20.9
Pongamia glabra (Karanja)	81.5	1.4630	113.4	1.4738	25.6
Azadirachta indica (neem)	81.9	1.4572	101.7	1.4643	20.7

[a] Iodine value determinations were carried out by the Rosenmund-Kuhnhenn method as modified by Planck, Pack, and Goldblatt (22).

[b] The diene value is expressed in terms of the equivalent number of centigrams of iodine per gram of the sample (23).

These products are light brown to reddish brown in color and exhibit a marked tendency towards polymerization and gelation.

Results and Discussion

Allylic bromination occurs through a free-radical chain mechanism (18, 19), and the bromo-derivative undergoes a thermal splitting into a molecule of hydrogen bromide and a compound containing a new double bond in conjugated position to the ethylenic or acetylenic bond initially present in the fatty acid. The free-radical process is favored in the case of

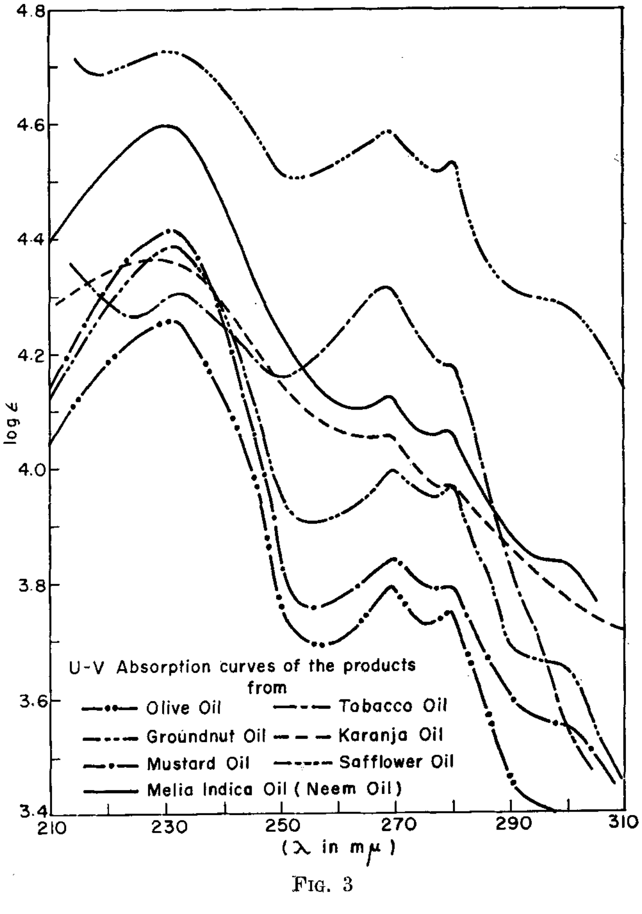

FIG. 3

allylic bromination with N-bromosuccinimide because catalysts, like ultraviolet light or peroxide (which are generally believed to catalyze reactions through free radicals), produce a pronounced effect on the rate of reaction with N-bromosuccinimide.

In the present study with methyl esters of fatty acids, products of all the bromination-dehydrobromination reactions showed blue fluorescence under ultraviolet light and a strong absorption maximum at 231 mμ (Figure 1). Furthermore the increases in iodine values, refractive indices, and diene values (Table I) clearly show that this method is at least 30 to 40% effective in creating a double bond in the conjugated position to the one initially present. The products polymerize and gel slowly.

By studying the reaction with methyl oleate, Sutton and Dutta (14) concluded that substitution of bromine for hydrogen took place on both sides of the double bond, possibly by a route other than a free-radical mechanism. In the present study, milder reaction conditions were used for the reactions of the methyl esters with equivalent amounts of N-bromosuccinimide. Consequently it was possible to prepare monobromo derivatives of the monoethylenic acids. Under these conditions, substitution might occur on either side of the double bond. Then, by thermal dehydrobromination, bromo-oleate might be converted to 9:11- and/or 7:9-octadecadienoate, bromopetroselinate to 6:8- and/or 4:6-octadecadienoate, and bromoerucate to 13:15- and/or 11:13-docosadienoate. The production of heptanoic acid by ozonization proved that the products from methyl oleate and erucate were, respectively, 9:11-octadecadienoic and 13:15-docosadienoic acids. In the case of methylpetroselinate the product was probably 6:8-octadecadienoic acid because ozonization gave decanoic acid, in agreement with earlier observation of Clemo and Stevens (15).

Thus our observations, as well as those of Clemo and Stevens (15) and Schmid and Lehmann (12), show that, in the reaction of equimolecular proportions of N-bromosuccinimide and a methyl ester of a monoethylenic acid, bromide tends to substitute by a free-radical process for hydrogen in the allylic methylene group farthest from the carboxylic group.

When an excess of N-bromosuccinimide by three to four times was used in the reactions with methyl oleate and erucate, the dehydrobrominated products included a small amount of material which exhibited ultraviolet absorption maxima at 231 and 268 mμ (Figure 2), indicating the presence of both diene and triene conjugation. All attempts to separate these products (by chromatography over silica gel) were unsuccessful.

By reaction with equimolecular proportions of N-bromosuccinimide and thermal dehydrobromination of the products, methyl stearolate and behenolate might be converted to 11-octadecen-9-ynoic and/or 7-octadecen-9-ynoic acids, and 15-docosen-13-ynoic and/or 11-docosen-13-ynoic acids, respectively. Conjugation of the acetylenic with an ethylenic double bond (20) was indicated by the absorption maximum at 228 mμ (Figure 1). The presence of an acetylenic bond was confirmed by the infrared absorption spectrum (21).

All the characteristics of the product from methyl stearolate (Table I) show that it may be methyl ximenynate or an isomer. Ozonization of the dehydrobrominated products from both methyl stearolate and behenolate gave heptanoic acid, showing that the products were 11-octadecen-9-ynoic and 15-docosen-13-ynoic acids, respectively.

From these results it is concluded that substitution of bromine in the allylic position generally takes place on the carbon farthest from the carboxylic group, in the acetylenic acids as well as in the monoenoic acids.

Characteristics of the products obtained from the application of this series of reactions to methyl 9:12-linoleate are shown in Table I. These are similar to those previously reported by Bergstrom and Hansson (16). The ultraviolet absorption spectrum (Figure 1) definitely shows triene and tetraene conjugation with a small amount of a diene-conjugated product.

Because the methylenic group at position 11 is activated, the major amount of bromination would be expected at this point. Subsequent dehydrobromination and rearrangement then would yield the triene-conjugated system. In addition, bromination might also occur at both positions 11 and 14, yielding a dibromo compound which would be dehydrobrominated to a tetraene-conjugated system. The presence of conjugated diene may be explained by a shift of double bonds during bromination. However no definite compound could be isolated from the products of ozonization.

When this series of reactions was applied to various oils, complete dehydrobromination could be effected only by heating in 2:4:6-collidine, pyridine, or quinoline. In this case the thermal dehydrobromination yielded gels unless one of these solvents was used. Characteristics of the original oils and the conjugated products are recorded in Table II. It is evident that the extent of conjugation of the oils was considerably less than that of the methyl esters. The ultraviolet absorption spectra (Figure 3) show the presence of both diene and triene conjugation in the products. Because the linoleate content of tobacco seed and safflower oils is high (66 to 70%), their products contained appreciable amounts of triene conjugation and gelled shortly after they were prepared. Their films set to the wrinkled patterns typical of tung and kamala oils.

Summary

a) A series of methyl esters of fatty acids were reacted with N-bromosuccinimide, and the products were dehydrobrominated by heating.

b) In the reaction of methyl erucate and methyl oleate with equivalent amounts of N-bromosuccinimide, bromination occurred in the allylic position farthest from the carboxyl group. Products of dehydrobromination contained 30–40% conjugated dienoic acids.

c) Use of excess N-bromosuccinimide led to production of both diene and triene conjugation.

d) Products from mono-acetylenic fatty acids had a double bond conjugated to the triple bond initially present.

e) The product from methyl 9:12-linoleate was a complex mixture having diene, triene, and tetraene conjugation.

f) Mustard seed, peanut, olive, karanja, neem, tobacco seed, and safflower oils were reacted with N-bromosuccinimide. The bromo derivatives could not be satisfactorily dehydrobrominated by heat alone; heating in pyridine, quinoline, or 2:4:6-collidine was more effective. The products from safflower and to-

bacco seed oils partially gelled during the process. The films of all the treated oils dried in wrinkled patterns.

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Methyl Esters Directly from Acidulated Soapstock

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THE ESTERS of fatty acids are usually prepared by alcoholysis of triglycerides or by esterification of fatty acids. As both of these commodities are in the 13¢ to 15¢-per-pound price range, esters prepared from them would necessarily be high in price. The use of acidulated cottonseed oil refinery soapstock (or foots) "as is" as a primary source of fatty acids for the preparation of fatty acid esters was suggested by the low cost of foots fatty acids (about 5¼¢ per pound) as compared to the distilled acids, by the fact that foots are normally in surplus and difficult to dispose of, and by the opportunity of making the fatty acid esters available at low cost for commercial uses.

Pack and Goldblatt (3) have reported a method of preparing benzyl esters by reacting the respective chlorides with dehydrated raw soapstock in an inert solvent media. However no work is known in which acidulated soapstock has been employed directly "as is" as the primary source of fatty acids for the preparation of the fatty acid esters. This paper is a report of the results of an investigation conducted to determine the conditions required to esterify *in situ* the fatty acids of acidulated foots and to develop a practical process for producing fatty acid methyl esters directly from acidulated cottonseed foots.

Experimental

Materials. Four lots of commercial grade acidulated soapstock (or foots) were used in this investigation. One lot had been hydrolyzed by the Twitchell process. All of the acidulated foots were from raw soapstocks produced by the continuous alkali-refining method. The analyses of the foots, given in Table I, show that their total fatty acids (T.F.A.) content varied only from about 91% to 94% but that their free fatty acids content ranged from 70% to 94%. This variation in free fatty acids was caused by the variation in neutral oil content, ranging from the unusually low value of 0.2% in the hydrolyzed foots to the rather high 23.2% in Lot A.

TABLE I
Analyses of Soapstocks

Lot	Description	Total fatty acids	Oxidized fatty acids	Free fatty acids	Neutral oil	Gossypol
		%	%	%	%	%
A	Acidulated	92.6	4.6	70.4	23.2	......
B	Acidulated	91.3	5.4	79.1	12.4	0.12
C	Hydrolyzed [a]	94.3	5.0	94.1	0.2	0.02
D	Acidulated	91.3	6.0	76.0	16.1	......

[a] Hydrolyzed by the Twitchell Process.

The methanol used was reagent grade absolute and was of synthetic origin.

Acidic catalysts were used because of their tolerance for small amounts of water, such as are found in most acidulated soapstocks. Hydrogen chloride was used as the catalyst in the first series of tests. The catalyst for all of the remaining tests was a crude form of Twitchell reagent in an excess of sulfuric acid. This catalyst was prepared by reacting together one mole of naphthalene, one mole of distilled cottonseed fatty acids (mixed), and 6 moles of 100% sulfuric. The resulting mixture of naphthalenestearosulfonic and sulfuric acid was used "as is." The sulfuric acid was probably the major catalytic agent with its activity enhanced by the emulsifying action of the sulfonic acid.

Methods of Analysis and Evaluation. The applicable methods of the American Oil Chemists' Society (1) were employed in determining total and oxidized fatty acids and unsaponifiable matter. Gossypol was determined by the method of Pons, Hoffpauir, and O'Connor (4) and neutral oil by the method of Linteris and Handschumaker (2) as modified by the American Oil Chemists' Society.

Free fatty acids in the distilled esters were determined by titration with 0.1 N alkali. The free fatty acids of the soapstocks were calculated on the basis of their content of total fatty acids and neutral oil.

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