Impurities in Vegetable Oil Refining Soapstock

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FOR the last decade, and particularly in recent years, foots from vegetable oil refining have held a most unenviable position in the trade. They cost the refiner too much to throw away even if the disposal problem were not such a difficult one; at the same time they are worth so little on the market that the refiner cannot afford to treat them except in the most economical manner. A partial solution to the problem has been obtained by acidulating to black acids, but this operation is marginal at best, as pointed out recently by Levin and Swearingen (10). The cost of acidulation seems to range from 0.6¢ to 1.0¢ per lb. of product, depending on the size, type, and location of the refiner and on the accounting method, but it is still an appreciable portion of the differential between standard grades of raw and acidulated foots. Moreover the impurities of the crude oil that are concentrated in the soapstock during refining are not generally removed during acidulation; these represent an economic loss in processing black acids. In fatty acid distillations it is reported that non-fatty acid impurities cause still pot losses by retaining up to their own weight in distillable fatty acids; operating time between still cleanings may also be reduced by an excess of impurities in the charge.

Normal economic trends in the industry have tended to increase the ratio of impurities to soap and neutral oil in the foots. The miller has contributed by increasing his overall yields in going from hydraulic pressing to expellers and then to solvent-extraction. The refiner has added to the problem by shifting to continuous processing and to refining-in-miscella. No abatement of the problem can be expected with current processing trends.

Nature of the Impurities

The term "impurities" has been used rather broadly in the discussion above, and, before proceeding further, some definition is desirable. Crude vegetable oils usually contain insoluble solids such as meal and metal oxides from the processing equipment; these solids are retained as bowl cake in any type of centrifugal refining and do not generally appear in the soapstock. Various types of non-glycerides and non-fatty acid materials have been reported in the literature as more or less soluble constituents of crude oils. These minor components are shown in Table I for crude cottonseed oils with approximate ranges for their probable content based entirely on literature sources.

TABLE I

Minor Constituents of Crude Cottonseed Oil

Component	Weight % on oil	Refr.
Gossypol	0.1-2	1, 3, 6, 14
Gossypol degradation products	0.2-1	1, 3, 15
Phosphatides	0.7-1.8	1, 2, 12, 16
Inosite phosphates	0.05	1, 2
Hydrocarbons	0.1-0.25	1, 2, 5
Phytosterols and phytosterolines	0.3-1.6	1, 2, 7, 11
Tocopherol	0.08-0.14	1, 2, 9, 13
Carbohydrates	0.1-0.25	1, 2, 8
Pigments	0.005	1, 2, 4
Miscellaneous	0.2-0.5	1, 2, 4, 7, 8

Most of these materials, except gossypol and its products, also appear in varying amounts in peanut, soybean, and coconut oils. Either caustic or soda ash refining is reported to remove the majority of these minor components although the hydrocarbons, sterols, and pigments are at best only partially removed. Soapstock, then, is comprised of neutral oil, saponified fatty acids, and these other materials which are largely impurities from the standpoint of the black acids user. At best, some of these, such as lecithin and cephalin in the phosphatides, may yield their fatty acid content under appropriate treatment, such as reaction with strong caustic.

Spence (17) suggested an analytical method used somewhat by the industry to separate quantitatively and quite reproducibly the impurities from the fatty acids. In the more recent work a basically similar procedure, Tentative A.O.C.S. Method G3-53, has been used for the analysis. In both cases the analysis depends on the differential solubility of fatty acids and impurities at high dilutions in petroleum ether. After saponification and acidulation of the sample as in A.O.C.S. Method G3-39, relatively pure fatty acids are removed by extraction with a large volume of petroleum ether, leaving the impurities behind. The latter may be split further by extraction with ethyl ether to give an ether-soluble fraction called "Oxidized Acid Impurities" and an insoluble fraction called "Insoluble Impurities." The term Oxidized Acids is not based on chemical composition but is retained from trade terminology for any type of non-fatty acid component with these general characteristics. While the refinements of the A.O.C.S. Tentative Method enhance its reproducibility, results obtained by the two methods are close and are used interchangeably in this study.

Method of Purification

The problem of impurities in cottonseed foots seemed particularly pressing when this investigation was started several years ago. Soybean foots generally showed a greater market demand with less tendency toward sub-standard quality. As a result, almost all of the work has been directed toward methods of improving the quality of cottonseed foots although a little work has also been done on peanut, coconut, and soybean soapstocks.

Table II shows representative analyses for raw cottonseed foots from expeller and hydraulic oils for both soda ash and caustic refining. Analyses of peanut foots from caustic and soda ash refining are also included as well as examples of soybean foots and kettle-refined coconut stock. The last column of the table shows the percentage of impurities on the basis of black acids composed of the total fatty acids plus the Oxidized Acids and the Insoluble Impurities. In general, it is seen that Oxidized Acids run 1-4% on foots, and the Insoluble Impurities somewhat less; total impurities range from 5-25% on black acids.

These impurities are not generally subject to attack by acids and, as a result, are but slightly removed during acidulation. Some of the Insoluble Impurities

TABLE II

Typical Analyses of Raw Foots

Crude Oil	Milling method	Refining method	TFA	Oxidized acids	Insoluble impurities	Impurities/ black acids (%)
Cottonseed	Hydraulic	Caustic	45-58	1.6-3.3	0.9-1.7	5-10
Cottonseed	Expeller	Caustic	35-50	2.0-4.7	0.6-1.7	8-14
Cottonseed	Hydraulic	Soda ash	25-35	2.1-3.9	0.6-2.3	13-17
Cottonseed	Expeller	Soda ash	19-33	1.3-5.0	1.0-2.2	13-25
Cottonseed	Calif. exp.	Soda ash	15	3.0	0.9	20.6
Peanut	....	Caustic	55	1.6	0.9	4.3
Peanut	....	Soda ash	23-28	1.1-1.6	0.5-2.1	6-13
Coconut	....	Caustic*	28	0.5	0.05	1.9
Soybean	....	Caustic	33	1.3	1.4	7.6

* Kettle refining.

are concentrated after settling at the mineral acid-black acid interface; these are eliminated only to the extent that any of the interface sludge may be run to sewer. An example of this interface concentration is shown in Table III, where analyses are given for a raw cottonseed soapstock and for the clean black acids and interface black acid sludge resulting from a laboratory acidulation of the foots; the high moisture contents do not affect the impurities content. The analysis of the mineral acid phase shows only a small amount of TFA and Oxidized Acids.

TABLE III

Impurities Distribution in Acidulation

Source of sample	Weight % in sample			
	TFA	Oxidized acids	Insoluble impurities	Impurities/ black acids (%)
Raw cottonseed soapstock	47.7	2.5	1.8	8.3
Black acids	81.0	5.0	2.3	8.2
Interfacial sludge	49.6	6.7	4.4	21.9
Mineral acid phase	0.2	Trace	0	....

These impurities are probably not destroyed or lost during Twitchell- or pressure-splitting and therefore are included in a still charge following these steps. If sufficient time is allowed in field storage tanks prior to distillation, it is probable that a portion of the Insoluble Impurities are eliminated by sedimentation because some of this material has a density greater than 1.0 g./cc.

Centrifuging the acidulation mixture on a laboratory scale showed excellent results in reducing moisture content of the black acids to a minimum but had little effect on impurities. Variations in laboratory acidulating techniques likewise showed no consistent improvement in impurities removal from one stock to another.

Since acid treatment is ineffective, processing with an alkali, such as caustic, is an economically feasible approach. Literature reports and a few laboratory tests showed that the constituents of the impurities are generally subject to degradation and reaction with caustic and that the solubility of the products should be fairly good in aqueous caustic. A slight excess of caustic above that necessary to complete saponification of neutral oils did not prove effective however in reducing the impurities even with very long processing times.

It was found that treatment of a diluted soapstock with sufficient caustic to saponify the neutral oil, digest or at least degrade the gums, and grain out a soap could effect a large reduction in the impurities content of the resultant soap. The procedure currently considered to be the most efficient is outlined in Figure 1. The soapstock is diluted with enough water to facilitate pumping; after thorough mixing and heating to 150-200°F., it is metered to a closed compartmented medium speed mixer containing heating coils. Caustic as 50% solution is added to the first compartment of the mixer, and the temperature in the mixer is maintained at about 200°F.; sufficient water is added to the last compartment of the mixer to control the grain of the soap for easy separation of the phases in a centrifuge. The mixture is then centrifuged to give soap and a lye phase with about 5-10% caustic and up to 1% dissolved TFA. As is common practice in preparing soapstock for soapmaking, this first stage soap may be dissolved in water and regrained with salt or caustic to effect an additional reduction in impurities. This procedure has been applied successfully to caustic and soda-ash refined hydraulic and expeller cottonseed stock, caustic and soda-ash refined peanut foots, and coconut foots; soybean stock has not yet been tested.

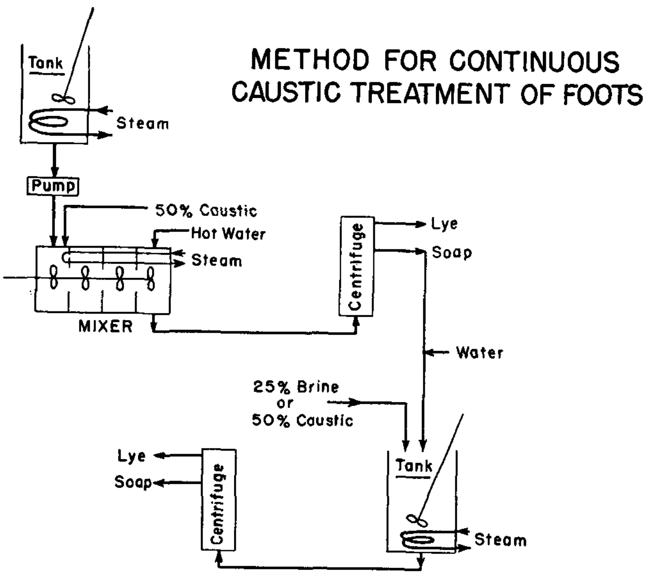

FIG. 1

The main variables of the treatment as outlined are the water/soapstock ratio, the caustic concentration, time and temperature of mixing, and the hardness of the final grained soap. The effect of these variables is apparent in the rate of graining in the mixer, in the cleanness of the centrifugal separation, and particularly in the TFA and the impurities ratio of the final soap. The scale and type of processing equipment, that is, laboratory batchwise and continuous or pilot plant continuous, makes little difference on the effects of the variables although continuous treatment generally requires a higher caustic concentration. Similarly, soapstock aged by shipping time requires less caustic than fresh soapstock.

Soap Quality

The effect of caustic concentration is most noticeable in soap quality, particularly with soda ash expeller cottonseed stock as shown in Table IV for first stage soap. It is seen that an increase in the concentration of caustic in the lye increases the TFA and decreases the impurities content of the soap; such a significant response to caustic concentration was not found for all stocks, as is shown in Table IV for a soda ash hydraulic cottonseed stock.

TABLE IV
Effect of Caustic Concentration on Soap Quality

Soapstock	% NaOH in lye	Soap, TFA	Total impurities/black acids (%)
Expeller	(Feed)	16.4	21.2
	4.7	37.1	15.8
	5.2	40.6	13.6
	5.9	55.1	7.0
Hydraulic	(Feed)	29.3	13.2
	9.5	32.9	12.9
	11.0	31.4	11.2
	12.8	32.2	10.6
	14.4	33.9	9.3

The water/soapstock ratio was not varied widely in this investigation; it is desirable to keep this ratio to a minimum to decrease the caustic consumption because caustic concentration and not total amount of caustic present appears to be the critical factor both in graining a soap and in reducing impurities. Increasing the water/soapstock ratio usually has the effect of decreasing the impurities ratio; this is primarily a solubility effect but probably also improves contact between the caustic and soap in the mixer. The first stage lye frequently carried up to 15% and 25% dissolved solids for caustic and soda ash stocks, respectively. Making allowance for the caustic, carbonate, and chloride salts in each case, these results show the lye carrying 5 to 10% of non-salt solids removed from the soapstock. Too low a water/soapstock ratio causes saturation of the lye with respect to some of these impurities as well as an increased salting-out effect of the electrolytes.

Mixing time was varied from 11 to 71 minutes on pilot plant continuous runs, and graining was achieved in every case. Table V shows one set of results for soda ash expeller cottonseed stock.

TABLE V
Effect of Mixing Time on Soap Quality

% NaOH in lye	Soap, TFA	Total impurities/black acids, %	Mixing time (min.)
(Feed)	22.8	30.3	....
19.5	48.0	11.4	51
19.7	40.5	12.4	24

This increase of TFA and decrease in impurities for increased mixing time was generally found for the continuous runs. Since the impurities are apparently carried with the soap phase as surface and intergranular adsorbates, the longer contact time with caustic may allow greater dissolution of the impurities in the lye phase. The temperature of the mixer was usually held constant at 200-205°F.; lower temperatures gave poorer quality soaps.

No consistent result was obtained in regard to color of the soap except that the soap product was always lighter to some degree than the soapstock. Expeller stocks particularly were lightened by the processing. A soap which was grained too hard tended to trap lye in fine streaks throughout the soap mass much like an intergranular layer. Lye thus trapped in the soap lowered the quality considerably although the TFA of the soap was often high.

Other reagents, such as sodium chloride or sodium sulphate, can be used with caustic to grain the first stage, but the soap quality is poorer than with caustic alone. This result can probably be attributed to a decreased solvent effect of the salt solutions compared to lye. Data are shown in Table VI for a soda ash expeller cottonseed stock and for the caustic-digested cottonseed stock mentioned previously.

TABLE VI
Effect of Graining First Stage With Salt

Soapstock	Lye phase concentrations (%)		Soap	
	NaOH	NaCl	TFA	Impurities/black acids (%)
Expeller	(Feed)	....	22.8	30.3
	16.9	0.2	48.2	10.9
	5.6	16.1	38.9	13.5
NaOH-digested	(Feed)	....	52.2	14.5
	8.0	0.1	61.3	6.2
	0.4	8.4	54.7	14.3

Graining Conditions

Some interesting results were found during a study of graining time, and these give an insight into the action of caustic on the gums. Since the size of the mixer required depends on the rate of graining as well as the overall mixing time desired, batch graining rates were studied on a laboratory scale. The rate of graining was determined by bottle centrifuging of samples taken at known times after the addition of caustic to an agitated soapstock-water mixture. It was found that a period of no grain formation followed the addition of caustic to the mix and this time was termed the induction period.

In general, the induction period was shortened by an increase in the water/soapstock solids ratio. This effect for three runs at about 7% caustic concentration is illustrated in Figure 2, where the induction

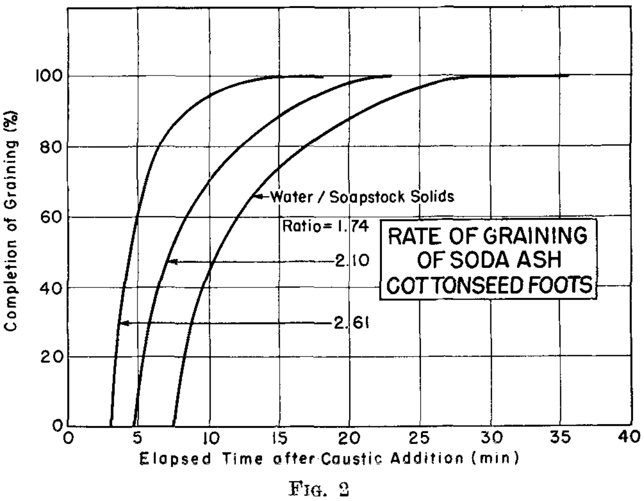

FIG. 2

TABLE VII

Impurities Content of Treated Soapstocks

Soapstock	Raw			First stage			Second stage		
	TFA (%)	OA*	OA+II	TFA (%)	OA	OA+II	TFA (%)	OA	OA+II
		BA	BA		BA	BA		BA	BA
Cottonseed, expeller, soda ash	24.8	....	....	33.6	10.2	13.4	54.5	4.9	9.2
Cottonseed, expeller, soda ash	21.8	22.2	27.1	48.0	10.3	11.5	58.0	2.0	6.1
Cottonseed, California expeller	15.3	15.9	20.1	36.9	10.9	16.5	51.8	9.1	14.5
Cottonseed, hydraulic, soda ash	26.1	9.1	15.5	37.4	4.3	8.6	55.4	2.3	6.3
Cottonseed, hydraulic, soda ash	29.3	6.7	13.2	32.2	5.2	10.8	44.6	4.9	9.3
Cottonseed, expeller, caustic	32.0	12.8	14.2	61.0	2.9	5.0	....	....	....
Cottonseed, hydraulic, caustic	47.7	6.5	9.1	50.0	4.6	8.7	....	....	....
Peanut, soda ash	24.6	7.7	14.6	40.0	....	....	47.3	3.4	5.2
Peanut, caustic	58.1	2.7	4.1	54.0	1.5	1.7	....	....	....

* OA = Oxidized Acids, II = Insoluble Impurities, BA = Black Acids

period is determined by the intercept of the rate curve with the time axis. The times for complete graining are in the same order as the induction periods and are roughly proportional to them.

Decreasing the caustic concentration at a constant water/soapstock solids ratio slightly reduced the induction period until the concentration was too low for good graining. The rate of graining was increased by increasing the temperature. Studies on the rate of saponification of the neutral oil indicated that this reaction proceeds rapidly in the presence of such large amounts of soap and is probably completed in less than a minute with good agitation.

The formation of soap miscelles is generally thought to occur quite rapidly when the conditions are right. Many types of materials, particularly surface-active ones, are known to inhibit crystal growth and might be expected to inhibit the graining of soap in a similar manner. Cottonseed stocks contain many degradation products, proteins, phosphatides, and sterols that are surface-active. Peanut stocks have fewer of these and also show shorter induction periods than cottonseed; a caustic-digested cottonseed stock probably contains mostly degraded impurities and does show almost no induction period. It appears then that the induction period is the time necessary for caustic to attack the impurities and degrade them sufficiently to solubilize them in the caustic solution and to allow graining of the soap phase. It also appears reasonable that salt or other electrolytes incapable of the caustic reaction cannot effect purification of the soap phase. In continuous operation in the pilot plant mixer with good temperature control, higher caustic and soap concentrations, and better agitation, graining times were apparently shorter than in the laboratory batch tests.

It is well known from the phase diagrams of pure and mixed fatty acid soaps with electrolytes and water that a grained soap should have a TFA of about 63% unless it is mixed with a niger phase. In this soapstock work no evidence was found for any phase other than lye and soap. The fact that soap phases obtained from this process have TFA values in the range of 30 to 60% must then be considered anomalous. The cause is not known, but it is thought to be due to surface adsorption of the impurities of the soap phase. Even though degraded, the impurities are still organic in character and cannot be fully soluble in the aqueous caustic. Theoretically sterols should not be removed from crude oil by alkali refining, but the fact that they are indicates an adsorption mechanism. The same condition probably exists in the caustic-treated soapstock mix but with the impurities in a far more surface-active form.

Results of Treating Foots

The primary effect of caustic-treating raw foots is to increase the TFA and to decrease the impurities content. A secondary but important result is to increase the ease of acidulation of the foots and, of course, to decrease the impurities content of the black acids made from the foots. Examples of soaps from one- and two-stage treats are shown in Table VII for several types of foots. Recent results on acidulation indicate that centrifuging of the acidulated mix from treated soapstock can eliminate most of the Insoluble Impurities from the black acids by use of a special skimmer in the centrifuge or by control of the aqueous phase density. For this reason, the percentage of impurities in black acids is given in Table VII both with and without the Insoluble Impurities fraction. For all soapstocks except California expeller cottonseed, the impurities ratio was reduced in one or two stages to less than 5%, excluding the Insoluble Impurities. Acidulated stock from the treated foots was very low in neutral oils. The regular neutral oil analysis included a large unsaponifiable fraction; after removal of the latter, the resultant neutral oil content ranged from 0.3 to 0.6%, but even this material was more waxy than oily.

A fairly sensitive test of the quality changes in the black acids due to prior treatment of the foots is afforded by a laboratory distillation. Several samples of first stage soap were acidulated without the special treatment mentioned above to remove the Insoluble

TABLE VIII

Laboratory Distillations of Cottonseed Black Acids

Soapstock	Soap		Dry black acids				Distillate yield, % of charge
	TFA	OA*	TFA	OA	II	OA	
		BA				BA	
Treated, expeller A	55.2	3.2	96.6	2.4	0.3	2.4	85.9
Treated, expeller B	53.6	6.1	98.1	1.9	0	1.9	88.7
Treated, hydraulic C	63.5	1.0	....	....	....	....	88.9
Raw, hydraulic C	34.8	6.5	....	....	....	....	69.7
Raw, hydraulic C	34.8	6.5	85.8	13.7	0.4	13.8	68.7

* OA = Oxidized Acids, II = Insoluble Impurities, BA = Black Acids.

Impurities. These black acids were distilled without Twitchell-splitting in a glass laboratory batch still at 6- to 12-mm. pressure. For comparison, untreated samples from raw cottonseed soda ash foots were acidulated, Twitchell-split, and distilled; the data for these tests are given in Table VIII. It is seen that the yield of distillate from a treated still charge was about 86-89% for both expeller and hydraulic stock; the latter stock in an untreated charge gave about 69-70% yield. Complete removal of Insoluble Impurities by centrifuging might increase by another 1% the yields from treated stock. In all cases the distillation was stopped when the distillate showed an appreciable yellow color, generally about 250-260°C. Insufficient data are available yet to relate still yields to the impurities ratio of the charge, but the results of Table VIII indicate roughly an inverse proportionality.

Summary

The nature of the impurities in vegetable oil foots renders them resistant to treatment by acids as in normal acidulation. Strong caustic was found to attack the gums and make them at least partially soluble in a 5 to 10% aqueous caustic solution. At this concentration a soap phase of 45-60% TFA could be centrifugally separated, and the majority of the impurities or their degraded products were discharged in the lye. The ratio of Oxidized Acids and Insoluble Impurities to the TFA was much lower in the soap than in the raw soapstock; the Oxidized Acids/Black Acids ratio could generally be reduced to 5% or less. This reduction in impurities was found to improve laboratory still yields markedly without the necessity of Twitchell- or pressure- splitting the black acids from treated stocks. Distillate yields of 86-89% were obtained from treated stocks, compared to 69-70% from untreated stocks.

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REFERENCES

1. Bailey, A. E., "Cottonseed" (1948).
2. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed. (1951).
3. Clark, E. P., J. Biol. Chem., *75*, 725 (1927).
4. Earle, F. R., and Detwiler, S. B. Jr., Oil and Soap, *18*, 117 (1941).
5. Fitelson, J., J. Assoc. Official Agr. Chem., *26*, 506 (1943).
6. Harris, W. D., *et al.*, J. Am. Oil Chemists' Soc., *24*, 370 (1947); *26*, 719 (1949).
7. Jamieson, G. S., "Vegetable Fats and Oils," 2nd ed. (1943).
8. Jamieson, G. S., and Baughman, W. F., Oil and Fat Ind., *1*, 31 (1924); *2*, 101 (1925); *3*, 153 (1926).
9. Lange, J. Am. Oil Chemists' Soc., *27*, 414 (1950).
10. Levin, H., and Swearingen, J. S., *ibid.*, *30*, 85 (1953).
11. Mattikow, M., *ibid.*, *25*, 200 (1948).
12. Olcott, H. S., Science, *100*, 226 (1944).
13. Quackenbush, F. W., *et al.*, Ind. Eng. Chem., *33*, 1276 (1941).
14. Royce, H. D., Harrison, J. R., and Deans, P. D., Ind. Eng. Chem., Anal. Ed., *12*, 74 (1940).
15. Royce, H. D., and Lindsey, F. A., Ind. Eng. Chem., *25*, 1047 (1933).
16. Schofield, C. R., *et al.*, J. Am. Oil Chemists' Soc., *25*, 368 (1948).
17. Spence, A., private communication (1951).

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Pyrethrum Synergists in Sesame Oil. Sesamolin, a Potent Synergist

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SESAME oil, obtained from seeds of the plant *Sesamum indicum* (L.), was found, to the exclusion of all other oils tested, to increase the insecticidal potency of pyrethrins (12). Haller and his co-workers (14, 15) fractionated sesame oil by molecular distillation and, from the two most active fractions, isolated sesamin, a compound exhibiting marked synergism with pyrethrins. By a systematic examination of compounds similar to sesamin, these workers made the very important discovery that the intact methylenedioxyphenyl group is essential for sesamin's synergistic activity (16). That optical activity had no appreciable effect on the synergistic activity of sesamin was illustrated by the fact that asarinin and isosesamin, optical isomers of sesamin, were equally effective pyrethrum synergists. As predicted by them, their discovery led to the development of synthetic synergists of commercial importance.

Haller and co-workers recognized that considerable synergistic activity remained after the removal of sesamin, as did subsequent workers (18). However no other synergists in sesame oil have been thus far identified. The present research was undertaken in an effort to identify in the oil any compound or compounds other than sesamin that exert any appreciable synergism with pyrethrins so that the synergistic action of sesame oil might be fully accounted for.

Experimental

To accomplish this purpose it was decided to fractionate the oil by means of chromatography. Since the work of Haller and co-workers indicated that the strongly ultraviolet-absorbing methylenedioxyphenyl group was essential for activity as a pyrethrum synergist, it was believed that it would be possible to detect and roughly estimate the presence of any synergist by following the ultraviolet absorbance of the eluate fractions. This proved to be true. Furthermore the technique employing ultraviolet absorbance ratios previously used in the separation of alkaloids could be used to isolate and identify pure compounds from zones that separated incompletely (3).

Chromatography of Crude Sesame Oil. Partition and adsorptive chromatography were tried. The best separations were obtained by the latter technique on silicic acid.

A chromatographic column 5.5 cm. inside diameter and 31 cm. long, fitted with a sintered-glass disk, was used. A slurry of 300 g. of silicic acid (Merck) in isooctane (Phillips pure grade redistilled) was introduced into the column in three portions. The column was prewashed with 400 ml. of 12% ethyl acetate (N. F. anhydrous redistilled) in isooctane followed by 200 ml. of isooctane. Forty grams of crude sesame oil dissolved in 150 ml. of isooctane was added to the