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]

FRANK C. PACK and LEO A. GOLDBLATT, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

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

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[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

suspended in the reaction medium was reacted with benzyl chloride, the reaction mixture was held at reflux 2 to 4 hrs., then cooled slightly and filtered while still warm (60–70°C.). The filter residues were washed with fresh portions of solvent. The filtrate, composed for the most part of solvent and crude benzyl esters, was then separated by distillation. The crude benzyl, methyl benzyl, and dimethyl benzyl esters of cottonseed oil fatty acids were prepared in this manner. No serious effort was made to fractionate the crude fatty acid esters. One pass through a 6-in. Vigreaux column constituted the full extent of ester purification in all cases since the objective at this stage of development was a cheap material with plasticizer properties.

TABLE I

Evaluation of Benzyl Esters as Plasticizers for Polyvinyl Chloride

50% Ester 50% (DOP)		Di-Octyl Phthalate
2920	tensile strength (p.s.i.)	2920
1580	100% modulus (p.s.i.)	1560
290	elongation (percent)	300
−45.0°C.	brittle point	−31.0°C.

50% ester blend compatible during first 30-day observation period.

Table I shows the plasticizer performance of a benzyl ester preparation produced as described above. Noteworthy is the reduction of the brittle point temperature in the case of the benzyl ester blend. Plasticizer evaluation was carried out as described by Magne and Mod (5). None of the crude ester preparations proved suitable as a primary plasticizer. Utility of such esters would therefore be limited to the field of secondary plasticizers. All the ester preparations were colored, the hues ranged from light yellow to deep red. Although this approach to increased utility for soapstock was discontinued at this point, certain aspects of the work merit additional investigation. German patent 268621 issued Nov. 14, 1912, to Badische, Anilin, and Soda Fabrik, and the work of Rueggeberg *et al.* (8) suggest the use of organic bases as catalysts for this general type of reaction. Without benefit of catalyst or the preliminary establishment of optimum reaction conditions, our yields ranged from 30 to 60%, based on the amount of fatty acid soap present in the raw soapstock. Investigation of the desirability, from the standpoint of plasticizer performance, of separating the various benzyl fatty acid esters is indicated. The color of the crude products could certainly be improved, perhaps even eliminated, by efficient distillation.

Destruction of Gossypol

Attention was next directed to the destruction of gossypol in soapstock. Acidulated soapstock has recently found its way into the feed industry. Added in relativly small amounts (0.5–2.0%) to dry meals, this hydrolyzed vegetable fat alleviates dust problems and aids pelleting operations. The gossypol content of raw and of acidulated soapstocks varies widely with source and with treatment. Analyses in this laboratory exhibit a spread from substantially zero to over 6%. The use of substantial amounts of either the acidulated or the raw soapstock in feeds revived interest in a rapid and economical method for getting rid of gossypol.

Destruction of gossypol in raw soapstock proved surprisingly difficult. Pure gossypol in an alkaline solution oxidizes readily in air (1). It was inferred then that air-blowing, plus a mild heat treatment, would suffice for the destruction of gossypol in raw soapstock. That such was not the case is evident from the data in Table II. Free and total gossypol were determined by modifications [3] of published methods (6, 7).

TABLE II

Effect of Heat Treatment (100°C.) Plus Air-Blowing [a]

	% Gossypol	
	Free	Total
Control	2.31	2.81
2 hours	1.90	2.71
4 hours	1.76	2.40
19 hours	0.48	0.96

[a] Air blowing at the rate of 5 cu. ft. per hour per pound of soapstock for the first 4 hrs. only.

Due, no doubt, to associated protective substances the gossypol in soapstock stubbornly resists air-blowing and prolonged heating even at 100°C. Some of the early contributors to the literature concerning the effect of gossypol on animals, notably Withers and Brewster (9), reported the efficacy of iron salts both for the prevention and treatment of gossypol toxicity. The thorough incorporation of relatively large amounts of iron salts in soapstock does, to be sure, inactivate significant amounts of gossypol as is shown in Table III. Predictably this would be a difficult operation to accomplish commercially. In the laboratory iron salts were incorporated into diluted soapstock with a high speed mixer. Table III shows data for ferrous sulfate heptahydrate, but the oxidation state of the iron is of little or no consequence for this particular purpose. Ferric salts are equally effective. Several permutations of the heat, iron salts, and air-blowing treatment were tried. None showed marked advantage so higher temperatures without either air-blowing or the addition of iron salts were investigated.

TABLE III

Effect of Added Iron Salts [a] Plus Heat Treatment at 100°C.

	% Gossypol	
	Free	Total
Control	2.31	2.81
0.5% (2 hrs. heating)	0.92	2.11
2.5% (2 hrs. heating)	0.76	1.45
5.0% (no heating)	0.17	2.35

[a] Ferrous sulfate heptahydrate.

The treatment of raw soapstock, which is roughly 50% water, at temperatures above 100°C. requires pressure equipment. Small pressure bombs made from standard pipe fittings were employed for the first experimental heat treatments at temperatures above the boiling point of water. A typical bomb consisted of a 6-in. length of ¾-in. pipe threaded on both ends; a pipe cap closed one end, a reducer, ¾ in. to ¼ in., and a dial type thermometer with a 6-in. stem and ¼-in. standard pipe thread fitting completed the closure of the other end. A 20-ml. rimless Pyrex test tube was used as a liner for the bomb. The bombs were loaded with about 30 g. of raw soapstock, closed, and immersed in a 1-gal. oil bath preheated some 20 degrees above the temperature intended for treatment of the bomb contents. The pipe devices worked satisfactorily, but the heat-up interval for the con-

[3] The modifications necessitated by the alkalinity of soapstock involved acidulation of the samples (0.5–1.0 g.) with acetic acid (1.0 ml.). These modifications were suggested by W. A. Pons of this laboratory.

tents was unreasonably long (about 8 min.) in contrast to the time (1-2 min.) required for the destruction of gossypol at 200°C. and above.

In order to circumvent the prolonged heat-up interval, use was made of a sample container that at first glance seems an unlikely high temperature-pressure device, namely a sealed glass vial. Heat-up intervals of less than 60 seconds were achieved, using the glass vials. The vials were prepared by sealing one end of a 2-in. length of 6-ml. Pyrex tube. Approximately ½ g. of soapstock was then introduced into the tube with a large bore hypodermic needle and syringe. This technique allows the vial to be filled easily and prevents smearing the upper walls of the tube at the point where the final seal will be made. For treatment the sealed vials, with about one-quarter of the total volume left as free head space above the soapstock sample, were immersed in an oil bath preheated to the requisite temperature. Dozens of the sealed vial experiments were carried out at temperatures up to 240°C. without a single failure from either thermal shock or internally developed pressure.

Table IV shows data obtained by the sealed glass vial technique for the heat treatment of raw, alkaline soapstock. Table V shows similar data for acidulated soapstock. Alkaline soapstock is far easier to free from gossypol by simple heat treatment than is acidulated soapstock.

TABLE IV

Effect of Heating Alkaline Soapstock at Temperatures Above 100°C.

	% Gossypol	
	Free	Total
Control	3.76	4.20
180°C. (4 minutes)	0.54	0.67
190°C. (4 minutes)	0.15	0.16
200°C. (4 minutes)	0	0
210°C. (2 minutes)	0	0
220°C. (1 minute)	0.30	0.44
220°C. (2 minutes)	0	0
240°C. (1 minute)	0.15	0.32

TABLE V

Effect of Heating Acidulated Soapstock at Temperatures Above 100°C.

	% Gossypol	
	Free	Total
Control	6.2	6.2
180°C. (4 minutes)	5.6	5.4
180°C. (8 minutes)	4.5	4.9
190°C. (4 minutes)	5.0	5.1
190°C. (8 minutes)	3.8	4.1
210°C. (1 minute)	5.8	5.7
210°C. (2 minutes)	4.6	5.1
210°C. (4 minutes)	3.6	4.0

Since presently there seems to exist no adequate substitute for feeding tests insofar as the evaluation of gossypol toxicity is concerned, a pilot plant scale heat heating device is being constructed for the preparation of amounts of material sufficient for this purpose.

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Castor Seed Proteins and Their Viscosities

B. N. JOSHI and J. P. VARMA, National Chemical Laboratory of India, Poona

INDIA produces oilseeds to the tune of 675,000 tons *per annum*, out of which the production of castor seeds accounts for 118,000 tons according to the average figure up to 1950. Except for some quantity of castor seeds which is exported, castor seeds are hydraulically pressed to remove oil, and the cake is partly exported and partly used as a fertilizer, especially for sugar cane crops. The castor seed meal is usually first expressed cold and then hot at higher pressures. The proteins of the cake get partly denatured during the course of hot-pressing. In this paper an attempt has been made to obtain white, high-grade, undenatured proteins from seed kernels prior to extraction of oil by the usual methods of pressing and solvent-extraction. Thus by the adoption of this process both good quality oil and undenatured, high-grade proteins will be obtained, which can be used as casein substitute.

Studies on the castor proteins date back to Ritthausen's period (1) when systematic work was carried out for the first time in 1857 on the isolation and nature of proteins from castor seeds, which was confirmed and largely supplemented by the more exhaustive work of Osborne and his associates in the Connecticut Agricultural Experiment Station (2).

Ritthausen's dialysis of the extract of deoiled castor cake with 10% sodium chloride yielded crystalline globulin 12.4%, composed of α-globulin coagulating at 86°C. and β-globulin coagulating at 96°C. The globulin thus obtained gave an analysis, arginine 13.19%, histidine 2.74%, and lysine 1.54%. In 1888 Stillmark (3) showed that castor meal also contained a toxalbumin called ricin to the extent of 1.5%. Later work by Spies and collaborators (4) have shown that the castor cake contains an allergic protein polysaccharidic fraction or "pentose" protein to the extent of 1.8%, which causes asthma on prolonged inhalation.

The work on vegetable proteins by different workers has indicated that the proteins of various oilseeds consist mainly of glutelins, α-globulins, and β-globulins; and there is a similarity of behavior on the part of proteins from various oilseeds although there could be differences in their properties. The proteins (1, 2) obtained from castor meal have been found to be almost similar in properties to soybean and peanut. Investigations on the peptization of castor seed proteins