TABLE VII

Organoleptic Evaluation of Soybean Oil Deodorized With Type 316 Stainless Steel

	Flavor Scores and Significant Difference[a]					
Sample pairs	204-205	204-206	204-207	205-206	205-207	206-207
Zero time[b]	7.9 + 7.1	7.9 + 8.6	7.9 + 7.5	7.1 ** 8.6	7.1 + 7.5	8.6 * 7.5
Three days' storage at 60°C	5.7 + 4.8	4.9 + 4.9	4.8 + 3.9	3.8 ** 5.8	4.5 + 5.0	5.9 + 5.0

	204	205	206	207
0 time peroxide value	0.21	0.28	0.18	0.24
Average peroxide value after 3 days' storage at 60°C	5.7	4.5	4.6	5.2
Average peroxide value after 8 hours' aeration at 98.5°C	70.3	97.0	65.3	75.5

Identification of Samples—Treatment of metal strips present during deodorization:

204—Control sample—no metal present.
205—Stainless steel cleaned with 5% aqueous caustic and rinsed with water.
206—Stainless steel from deodorization 205 stored 3 days and cleaned with refluxing acetone-toluene mixture.
207—Stainless steel polished with No. 500 grit, cleaned with 5% aqueous caustic and rinsed with water.

[a] Method of Moser, Jaeger, Cowan, and Dutton, J.A.O.C.S. *24*, 291, 1947.

[b] All four samples were tasted at one time to obtain the zero time flavor scores. + = no significant difference; * = a significant difference; and ** = a highly significant difference.

Sample 206 was deodorized with strips of type 316 stainless steel present which previously had been used in a deodorization and then stored 3 days at room temperature, followed by cleaning in a Soxhlet extractor with an 80-20 acetone-toluene mixture. The sample of oil was given the highest initial flavor score, and after 3 days' storage at 60° C. it was scored as being better by a highly significant difference than Sample 205, an oil deodorized in the presence of strips of caustic-cleaned stainless steel. It is of interest to note that polishing alone was fairly effective in preventing contamination of the oil by metal.

Summary

With mild agitation, soybean oil is not appreciably contaminated by contact with clean steel surfaces unless the fatty acid content is above 0.1% and the temperature above 150°C.

It has been shown that an oxidized oil film is an effective coating for metals used in the construction of pilot-plant deodorizers. Such a film, to be most effective, should be washed free of unoxidized, noncoherent oil with a suitable solvent. If the metal is properly coated an oxidation-stable and flavor-stable oil can be obtained from the deodorizer, providing the oil has been properly refined and bleached. The oil film is nearly the equivalent of a glass surface in its effect on oil stability, is easily formed on a metallic surface, and can be readily removed when the metal is cleaned with caustic.

A silicone varnish film baked on the metal surface is somewhat less effective than an oil film. Other methods of treating steel or stainless steel, which include coating the metal with a polymeric ether-linked wax, grit-polishing, and electropolishing, are fairly effective in reducing corrosion of the metal during deodorization.

Acknowledgment

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Alcohols From Menhaden Oil by Sodium Reduction

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IN the classical Bouveault-Blanc procedure for the reduction of esters, large excesses of both sodium and reducing alcohol are used (10). Recent modifications in the process however have lowered the quantities of sodium and alcohol required to nearly the theoretical amounts (4). These improvements have increased interest in the application of the sodium reduction method to the commercial production of fatty alcohols from natural oils (6).

The sodium reduction of saturated glycerides, coconut oil for example, is being carried out on a commercial scale. This is made possible not only by the improved efficiency in the use of sodium but also by the ease of recovery of caustic soda and glycerol. Moreover, when it is desired to preserve the ethylenic unsaturation in alcohols derived from unsaturated glycerides, as cotton seed and sperm oils, the sodium reduction process offers a possible route. Catalytic hydrogenation of an ester for the most part simultaneously saturates these olefinic linkages.

The reduction of the polyunsaturated esters occurring in highly unsaturated vegetable and fish oils to produce alcohols with one or more double bonds per molecule has never been fully investigated. A

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[1] Presented at the 23rd Fall Meeting of the American Oil Chemists' Society at Chicago, Ill., on November 1, 1949.

study of the sodium reduction of such a system therefore was undertaken. Menhaden oil was particularly suitable for this study because of its low cost and high degree of unsaturation. The alcohols derived from menhaden oil, of higher molecular weight than those from coconut oil, should be of considerable interest because of the reaction possibilities associated with the double bonds as well as the hydroxyl group.

In the present work the alcohols obtained by the sodium reduction of menhaden oil were examined by ultraviolet spectrography to determine the degree of conjugated unsaturation present. A relatively saturated C-14 to C-16 fraction was separated by distillation from the menhaden alcohols to yield a mixture of C-18 to C-22 alcohols, averaging nearly two double bonds per molecule. This highly unsaturated alcohol fraction was selectively hydrogenated to a product averaging one double bond per molecule.

The Composition of Menhaden Oil. The composition of menhaden oil as given by Armstrong and Allen (1) (Table I) is in good agreement with that reported by Stingley (7). The latter however does not report the degree of unsaturation.

TABLE I

Component Acids of Menhaden Oil (1)

No. of Carbon Atoms	Acids, Weight %	
	Saturated	Unsaturated
14	5.9	
16	16.3	15.5(−3H)
18	0.6	29.6(−4H)
20	0.6	19.0(−10H)
22	0.8	11.7(−10H)
Total	24.2	75.8

The actual fatty acid chain length distribution was not investigated in the present work. The degree of unsaturation found in the alcohols obtained by sodium reduction is somewhat lower than that reported by Armstrong and Allen for the corresponding acids. The saturated components are concentrated in the C-14 to C-16 range, and the C-14 and C-16 alcohols can be separated from the C-18 to C-22 polyunsaturated alcohols by fractional distillation of the sodium reduction product.

The Sodium Reduction of Menhaden Oil. The sodium reduction process used was that described by Hansley (4). The menhaden oil, dissolved in a solution of the reducing alcohol in xylene, was added gradually to sodium suspended in refluxing xylene. Methyl isobutyl carbinol is particularly suitable as reducing alcohol, and it is readily available. After the reduction the reaction mixture was hydrolyzed by slow addition to an excess of boiling water. The organic larly was separated from the aqueous caustic layer, and the former distilled.

Four mols of sodium and two mols of reducing alcohol are required for each ester equivalent, as shown by the equation below.

Undesirable side reactions result from the direct reaction of sodium with the reducing alcohol and with any free acid or water which may be present as impurities. The amount of hydrogen generated by these reactions is then a rough measure of the inefficiency of the reduction. Other side reactions which may take place involve bi-molecular condensations and result in the formation of acetoacetic ester-type compounds and acyloins.

Light cold pressed menhaden oils (Samples E, F, and G) as well as crude menhaden oils (Sample A) were reduced with sodium. The typical results of a number of experiments on each type of oil are given in Table II.

TABLE II

Sodium Reduction of Menhaden Oil

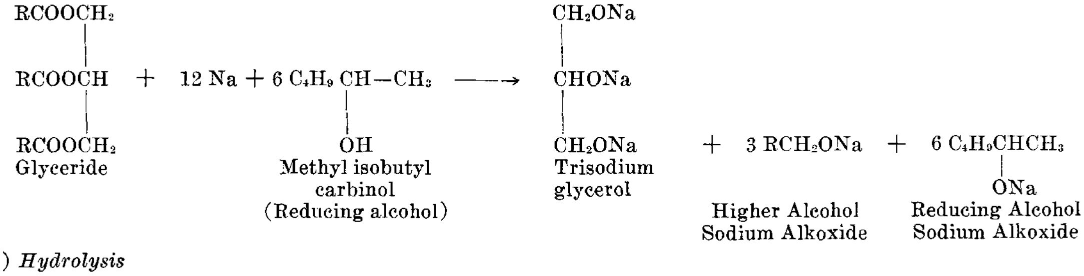
Menhaden Oil			Product		
Sample	Sap. No.	Iodine No.	Acid No.	Iodine No.	Yield Wt.%
A	199	188	0.0	176	86.4
E	199	193	15.2[a] 0.0[b]	168 161	85.8 85
F	191	164	0.0	153	87.8
G	201	200	11.8[a] 0.0[b]	179 170	86.2 88.6

[a] Product distilled from acidified crude alcohols.
[b] Product distilled from sodium soaps of by-product fatty acids.

The sodium efficiency averaged about 95% based on by-product hydrogen formed during the reduction process. Sodium is consumed in certain reduction reactions which produce acyloins so that indirect yields as determined by hydrogen evolution are higher than the yields calculated from the weight of alcohols isolated.

The unsaturated higher alcohols produced were light yellow in color and had much milder odors than the original oils. The iodine numbers of the products were slightly lower than expected. This apparent decrease in unsaturation may be partially due to some rearrangement of olefinic linkages to a conjugated structure during the reduction step with subsequent partial hydrogenation of the double bonds.

a) *Reduction*



$$\begin{array}{l} RCOOCH_2 \\ \quad | \\ RCOOCH \\ \quad | \\ RCOOCH_2 \end{array} + 12\,Na + 6\,C_4H_9\underset{\underset{OH}{|}}{CH}-CH_3 \longrightarrow \begin{array}{l} CH_2ONa \\ | \\ CHONa \\ | \\ CH_2ONa \end{array} + 3\,RCH_2ONa + 6\,C_4H_9\underset{\underset{ONa}{|}}{C}HCH_3$$

b) *Hydrolysis*

$$RCH_2ONa + H_2O \longrightarrow \underset{\text{Free Higher Alcohol}}{RCH_2OH} + NaOH$$

It has been shown that sodium does reduce conjugate unsaturation when the latter is present in the glyceride (4). Moreover it is well known that iodine number determinations on conjugated systems are not quantitative. There was also some polymerization of the polyunsaturated alcohols during distillation, and this would tend to decrease the amount of unsaturation found in the product alcohol distillate.

When the distillation of the crude product alcohol was carried out from the sodium soaps of trace amounts of fatty acids, the acid number of the product was zero as in (b) Table II. Most of the sodium soap by-product (formed by hydrolysis of traces of unreduced esters) remains in the organic layer during the washing step as a result of its low solubility in water. When the crude alcohol mixture was acidified before distillation, the regenerated fatty acids carried over during the distillation, as in (a) Table II.

Conjugation of the Double Bonds. The examination of the original glycerides and of the resultant alcohols by ultraviolet spectrography showed that some isomerization of the double bonds to a conjugated system was taking place during the sodium reduction step (Table III).

TABLE III
Conjugation in Menhaden Oil and Derived Alcohols

Sample	Iodine Value	% Alcohols With Conjugated Double Bonds		
		2	3	4
		%	%	%
Glyceride:				
A	188	0.9	0.2	0.05
E	193	1.4	0.2	0.05
F	164	0.9	0.2	0.07
Alcohols:				
1	159	15.7	5.5	0.8
2	153	10.8	4.1	0.6
3	144	8.6	3.4	0.5
4	98	0.2	0.02	0.00

The original glyceride contained only a minor amount of conjugation. The reduction product however contained 10-15% of alcohols having two conjugated double bonds and 4-5% of alcohols having three conjugated double bonds. Partial hydrogenation of the alcohol having an iodine value of 153 to an iodine value of 144 reduced conjugation to some extent. Hydrogenation to an iodine value of 98 practically eliminated all conjugation. Approximate calculations show that nearly 50% of the hydrogen taken up by the alcohol must have reacted with the conjugated double bonds. About 85% of the total hydrogen absorbed would be required to saturate the 15% of conjugated polyolefinic material indicated. As will be shown below, only about a half of the polyolefinic material is conjugated.

Little or no change in conjugation was noted as a result of distillation of the product crude alcohol from the sodium soaps. This would tend to indicate that the molecular rearrangement to the conjugated structure must have occurred during the reduction process itself. An experiment was carried out in which the time of contact of the alcohols with sodium and sodium alkoxides was reduced to a minimum (50 minutes compared to the usual 90-100 minutes) in the hope of reducing the amount of conjugation. There appeared to be some decrease in the amount of conjugated material, but the difference was not great enough to be conclusive.

Attempts to increase the amount of conjugation in the menhaden alcohols by heating in the presence of sodium methoxide were partially successful (Table IV). Apparently at the higher temperatures (200-250°C.) heat polymerization occurs which results in a decrease in the number of conjugated double bonds. This is indicated by the lowered iodine values.

TABLE IV
Isomerization of Menhaden Alcohols

Temp. °C.	Time (Hr.)	Iodine Value	% Alcohols With Conjugated Double Bonds			Isomerization % of Theory
			2	3	4	
......	0	156	14.6	4.0	0.2	46
195	2.5	134	19.1	3.8	0.5	78
235	2.0	127	10.2	1.5	0.2	....
226	4.0	128	11.1	1.7	0.1	....

An attempt was made to determine by calculation the percentage of the total polyolefinic material which possessed conjugated double bonds (Table IV). Apparently about half the polyunsaturated material with isolated ethylenic bonds underwent isomerization to conjugated structures during the reduction step. Previously reported work of Kass *et al.* (5) indicated that about half of the linoleyl alcohol prepared by the sodium reduction of methyl linoleate was in a conjugated form. The calculations here were based on the assumptions, a) that iodine values quantitatively represented the degree of unsaturation, b) that there was no saturated higher alcohols present, and c) that all the alcohols had the same carbon chain length.

Hydrogenation of Menhaden Alcohols. It seemed desirable to prepare from these complex mixtures, originally containing saturated, mono-olefinic, and polyolefinic alcohols, a more uniform mixture of alcohols containing one to two double bonds per molecule. Attempts were made to hydrogenate selectively the polyunsaturated alcohols in a mixture of mono- and polyolefinic alcohols. This has been done on mixtures of unsaturated acids (8).

The alcohols were first subjected to fractional distillation to remove most of the lower boiling saturated alcohols (Table V).

TABLE V
Distillation of Menhaden Alcohols (I.V. = 149)

Fraction	Boiling Range °C.	Pressure, mm. Hg.	Weight % of Alcohols	Iodine Value
I	170-193	14	15.6	46
II	193-196	14	8.1	62
III	170-230	0.1	70.3	172
Residue	230+	....	4.0	....
Total			98.0	

Fraction III (iodine value 172) was then subjected to hydrogenation with 3% Raney nickel catalyst at atmospheric pressure and a temperature of 25-60°C. Partial hydrogenation to an iodine value of 162 gave a product which had an improved odor but which was still yellow in color. Further hydrogenation to an iodine value of about 100 gave a colorless product having a characteristic "hydrogenation" odor. An iodine value of 162 would correspond to approximately 1.75 double bonds per molecule, and an iodine value of 100 to approximately 1.1 double bonds per molecule.

Only a relatively minor proportion of the higher alcohol was completely saturated during the hydrogenation. This was indicated by the small amount of saturated material precipitated by a single fractional crystallization from acetone at 0°C. (Table VI).

TABLE VI

Fractional Crystallization of Menhaden Alcohols From Acetone

Iodine Value	Precipitate		Filtrate	
	Wt.	Iodine Value	Wt.	Iodine Value
	%		%	
172	9.1	89	90.9	177
103	13.6	35	86.4	132
23	69.3	21	30.7	52

In another experiment, hydrogenation was carried out on the whole alcohol, i.e., before the saturated material was removed by distillation. The iodine value was first lowered from 163 to 144. Fractional distillation of part of this product gave the results shown in Figure 1.

Further reduction of undistilled material to an iodine value of about 100 gave a colorless product free of "unsaturated" odor.

It should be noted that the decrease in iodine value for the lower boiling, more saturated fractions was less than half the decrease in iodine value for the higher boiling, more unsaturated fractions. This, again, was evidence that selective hydrogenation of the polyunsaturated material had occurred to a relatively major extent.

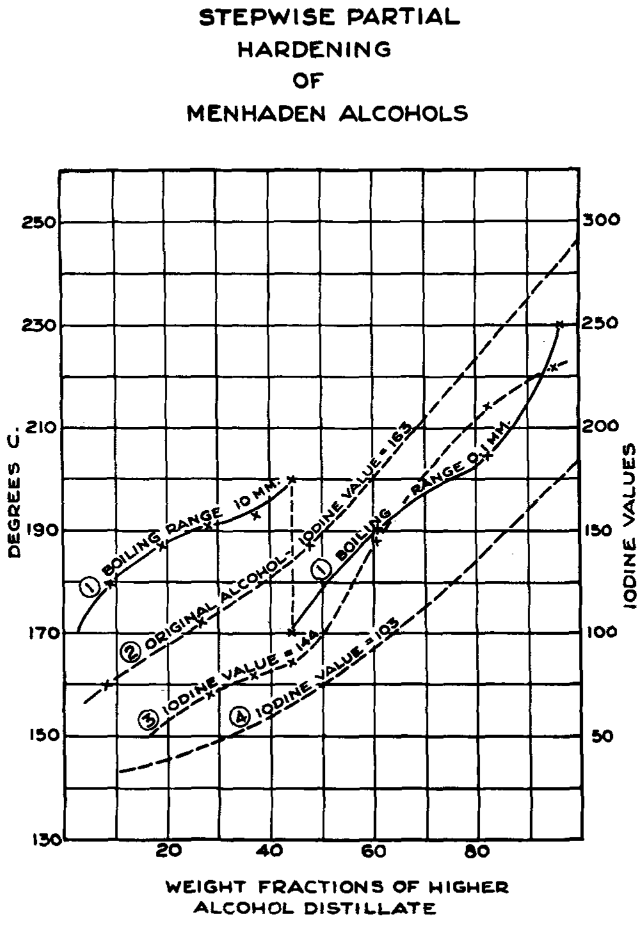


Fig. 1.

Experimental

Sodium Reduction Procedure. The menhaden oils used had acid numbers of five or less and iodine values of 160 to 200. They were dark yellow in color and had pronounced fishy odors.

The laboratory apparatus used was that described and illustrated by Hansley (4). A typical reduction was carried out as follows:

A small quantity of xylene (50-100 cc.) was placed in a three-liter, three-neck flask, fitted with a stirrer and a copper coil condenser, and heated to reflux. Freshly cut sodium (164 g., 7.14 mols) was then introduced. The xylene used in the reaction flask at the start was only sufficient to purge the reaction flask of air when at the reflux temperature. The menhaden oil, 500 g. (1.7 g. equiv.), was dissolved in 700 g. of xylene after which about 100 cc. of the xylene was removed by distillation to dry the mixture. To this glyceride solution 383 g. (3.75 mols) of dry methyl isobutyl carbinol was added. This solution was placed in the reservoir and introduced at a uniform rate into the reaction flask. The rate was adjusted so that all would be added in about 45 minutes. This rapid reaction rate was made possible by the use of the high capacity copper coil reflux condenser. The reaction heat was then removed by refluxing xylene. Stirring was continued for another 30 minutes after the addition was complete. Generally a small amount of sodium remained dispersed throughout the reaction mixture. The amount of hydrogen formed by side reactions was measured as it was evolved by means of a wet-test meter.

After the reduction reaction was complete, the reaction mixture was hydrolyzed by the introduction of small amounts through a funnel into a hydrolysis unit in which water was maintained at the boiling point of the xylene-water mixture. The hydrolysis unit consisted of a three-liter, three-neck flask equipped with a steam inlet, an outlet to a foam trap, and a return from the trap (4). A high capacity copper coil condenser was mounted at the outlet from the foam trap. The small amount of unchanged sodium present in the reduction reaction mixture was decomposed smoothly during this procedure.

The total amount of hydrogen liberated during the reduction and hydrolysis steps was 7.01 liters (STP). After correction for the excess sodium used, the amount of hydrogen representing wastage reactions was 3.20 liters (STP). This was equivalent to 4.2% of the sodium theoretically required for the reduction. The sodium efficiency was therefore 95.8%.

When most of the organic solvent had been removed by steam distillation, the aqueous and organic layers were allowed to separate, and the former was removed by syphoning. The organic layer was then washed twice with saturated brine in the hydrolysis vessel, using live steam for agitation. The organic layer was then distilled at reduced pressure to give 393 g. of distilled higher alcohols. This corresponded to a yield of 86.5%, based on the original glyceride. The non-volatile residue amounted to 47 g. The traces of fatty acids present in the crude alcohol were held back as the non-volatile sodium soaps. If a salt solution is not used during the washing step, the soaps and higher molecular weight free alcohols present sometimes cause emulsification which makes the separation of layers difficult. Methanol, to the extent of 5-10% by volume, will also prevent emulsification at this stage. Acidification with a mineral acid will cause sharp separation of the liquid layers, but the product obtained upon distillation will contain whatever fatty acids were present in the original oil together with fatty acids formed by saponification of any unreduced glyceride during the hydrolysis step.

The iodine values of the alcohols were determined with Wijs reagent. A reaction time of about two hours was used in this determination.

Ultraviolet Analyses. A Cary recording spectrophotometer was used to determine the ultraviolet absorption of the unsaturated alcohols dissolved in absolute ethanol. Absorption bands characteristic of two to six conjugated double bonds were detected. Five and six conjugated bond types were present in only trace amounts. The percentage transmissions were read at 233, 281, 270, 320, and 307 millimicrons as recommended by Bradley and Richardson (2). The average wavelengths at which maximum absorption actually occurred were at 233, 279, 269, 316, and 301 millimicrons. The amount of conjugation was estimated by calculation from the ratio of the specific extinction of the sample to the specific extinction of the pure conjugated C-18 acids as given by Bradley and Richardson. No attempt was made to correct for background absorption of the carboxyl group or for the effect of the background absorption of the triene or tetraene on the diene or triene, respectively (3). Since no pure alcohols with conjugated bonds were available for use as reference standards, the specific extinctions of the conjugated C-18 acids were used. Therefore the results can be considered to be semi-quantitative only. Interference due to trace amounts of xylene would not be appreciable (9).

Hydrogenation. The menhaden alcohol and 2-3% Raney nickel catalyst were placed in a three-liter, three-neck flask equipped with an air-driven stirrer, a nitrogen inlet, a hydrogen inlet, and an outlet connected to a wet-test meter. The flask was immersed in a water bath. Absorption of hydrogen was sufficiently rapid for partial hydrogenation purposes over the temperature range from 25-60°C. After the apparatus had been flushed with nitrogen the hydrogen was passed into the flask slowly through a calibrated rotameter while the contents were being stirred rapidly enough to fill the flask with a fine spray. In this manner it was possible to feed a predetermined amount of hydrogen and to stop the hydrogenation at any point to give a product with the desired amount of residual unsaturation.

Summary

Menhaden oil, a low cost fatty acid glyceride containing a high percentage of polyunsaturated material, has been reduced by means of sodium with 86-88% yields of alcohols having a correspondingly high degree of unsaturation. It has been shown that about one-half of the polyolefinic unsaturation isomerized during the sodium reduction to conjugated double bonded structures. The higher unsaturated alcohols were selectively hydrogenated to give a colorless product which was substantially odorless and which had an average of one double bond per molecule.

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Preparation and Utilization of Cottonseed Meal Glue for Plywood[1]

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THE utilization of cottonseed meal or cake in the preparation of plywood glues has been reported in the patent literature (1,7-12,14,16-18). These patents are concerned primarily with glue formulation and do not give processing data for the preparation of plywood using cottonseed meal glue or shear strength data for the glue joints. Other publications on the viscosity characteristics of cottonseed protein dispersions have indicated that the viscosity of the dispersions tend to decrease as the dispersions are aged (2,6). These articles indicate the unique viscosity properties of cottonseed protein as compared to other vegetable proteins whose dispersions usually increase in viscosity as they are aged. Consequently the possibility of developing a cottonseed meal glue with a long "working life," i.e., a dispersion having low viscosity for several hours, seemed likely.

The purpose of this report is to present data on the formulation of cottonseed meal glue, processing information for the preparation of plywood using the glue, and shear strengths of the glue joints.

Experimental

Cottonseed Meals. The hexane-extracted meal was prepared by removing the oil from flaked cottonseed meats by means of commercial hexane as described in a previous publication (15). The hydraulic-pressed and screw-pressed meals were prepared by express-

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