Synthesis of Wax Esters for Use as Possible Sperm Oil Replacements[1]

ABSTRACT

In efforts to prepare wax esters chemically similar to those comprising sperm oil, selected fats or blends thereof were reduced to alcohols which then were reacted with the initial triglycerides to get such wax esters. For instance, lard oil was reduced to lard oil alcohol in the presence of sodium and methyl isobutyl carbinol in xylene. Most of the resulting sodium alcoholates (95-98%) were decomposed with urea, and subsequent addition of lard oil (triglycerides) resulted in rapid formation of the desired wax esters in ca. 80-90% yields. In preliminary studies, the same wax esters were prepared by a more circuitous route. The alcoholates were decomposed completely with urea, the fatty alcohols were liberated, and they then were esterified with free lard oil acids. Similarly treated were a blend of lard, coconut and crambe oils, fractionated tallow, and a commercial grade oleic acid.

INTRODUCTION

The U.S. ban on the importation of sperm whale oil prompted our search for a low cost method of synthesizing a substitute with similar physical and chemical properties that could replace it in most of its wide variety of uses. Sperm whale oil is a unique mixture comprised of 15-25% triglycerides and 75-85% wax esters. The wax esters range from C_{24}-C_{44} in chain length and equal palmitoleyl or oleyl oleate in degree of unsaturation and average mol wt. Therefore, our efforts were geared to preparing such wax esters from inedible fats and oils for possible use as sperm oil substitutes and to providing a new outlet for some agricultural commodities. To meet these aims it was necessary to select a procedure suitable for the preparation of wax esters in sufficient amounts for evaluation in comparison with sperm whale oil. Among the variety of routes considered for the preparation of such wax ester mixtures were the direct esterification of suitable fatty acids, and the alcoholysis of triglyceride blends with monounsaturated fatty alcohols. These methods, however, were precluded by the unavailability at a reasonable cost of the required unsaturated alcohols, since these previously were obtained mainly from the very sperm whale oil that is now in short supply. Other pathways to wax esters are those involving the catalytic, high pressure hydrogenolysis of a variety of fatty starting materials. These hydrogenolysis procedures, however, could not be evaluated at this laboratory because of the lack of proper equipment. Furthermore, these methods, when applied to unsaturated fats, may yield solid wax esters instead of the desired liquid ones, since hydrogenolysis reactions are known to entail varying degrees of double bond reduction and *cis*- to *trans*-isomerization. Hence, the route chosen was a modified Bouveault-Blanc reduction (1-3) of triglycerides followed by esterification of the resulting alcohols with fatty acids obtained from the same triglycerides by hydrolysis. The known retention of double bonds and of their geometric configuration afforded by this route was an important factor considered in its selection. The use of urea, instead of water, for decomposition of the sodium alkoxides formed in this reduction of esters was resorted to in the interest of convenience and safety during these laboratory preparations. Moreover, the value of the concurrently formed sodium cyanate possibly could offer potential abatement in cost of the wax esters produced via this route.

Nonpolar, high mol wt unknowns produced during the sodium-alcohol reductions proved to be wax esters and led to the phase of our work that culminated in a more direct and potentially more economical process for the preparation of wax esters. The nature and details of this more direct route also will be discussed.

EXPERIMENTAL PROCEDURES

Materials

Lard oil, coconut oil, and oleic acid (Groco 5-L) were obtained from commercial sources and used as received. Crambe oil was obtained from the Industrial Crops Laboratory, NRRC, USDA, Peoria, Ill., and oil mix A was a blend of 64% lard oil, 19.2% coconut oil, and 16.2% crambe oil. Tallow oil, a liquid fraction from the solvent fractionation of tallow (4), was obtained from the Physical Chemistry Laboratory, ERRC, USDA, Philadelphia, Pa. The sodium (for the reduction reaction) was scraped free of any coatings and comminuted prior to use. Methyl isobutyl carbinol (MIBC) and all other reagents and solvents were used as received from commercial suppliers. The iodine values, saponification numbers, and acid numbers of the oils and of the MIBC esters of oleic acid were as follows: lard oil, 74.7, 195.7, and 3.6; coconut oil, 8.8, 249.8, and 1.0; crambe oil, 94.7, 195.4, and 2.4; oil mix A, 65.8, 202.2, and 3.0; tallow oil, 62.4, 194.4, and 2.3; and MIBC-oleate, 66.1, 162.8, and $\sim$ 0.8. The oleic acid (Groco 5-L) had an iodine value of 88.5, acid no. of 197.5 and sap. no. of 205.5.

Assay Methods

Thin layer chromatographic (TLC) examination of products was made on 25 mm silica gel coated plates. These usually were developed in 1:29:70 parts methanol:benzene:n-hexane solution, sprayed with 75% H_2SO_4 saturated with $K_2Cr_2O_7$ and heated for visualization. Gas liquid chromatography (GLC) of products was carried out on a Hewlett-Packard F&M 700 instrument equipped with a thermal detector usually held at 330 C and injection port at 280 C. The 6 ft x 1/4 in. columns were packed with 60-80 Diatoport S or 80-100 mesh Chromosorb W support coated with 10% SE-30 stationary phase and were eluted with 60 ml/min helium. The column temperature was programed at 2 C/min from 160-300 C and held isothermally thereafter. Liquid film IR spectra were obtained on a Perkin-Elmer model 237 instrument. IV were obtained by Wijs method, acid numbers by standard or microprocedures, and samples for saponification numbers were heated for 4 hr instead of usual 1 hr to ensure complete reaction.

Procedures

The apparatus used for the reductions is shown in Figure 1. Its important features are the high torque mechanical

[1]Presented at the AOCS Meeting, New Orleans, April 1973.
[2]ARS, USDA.

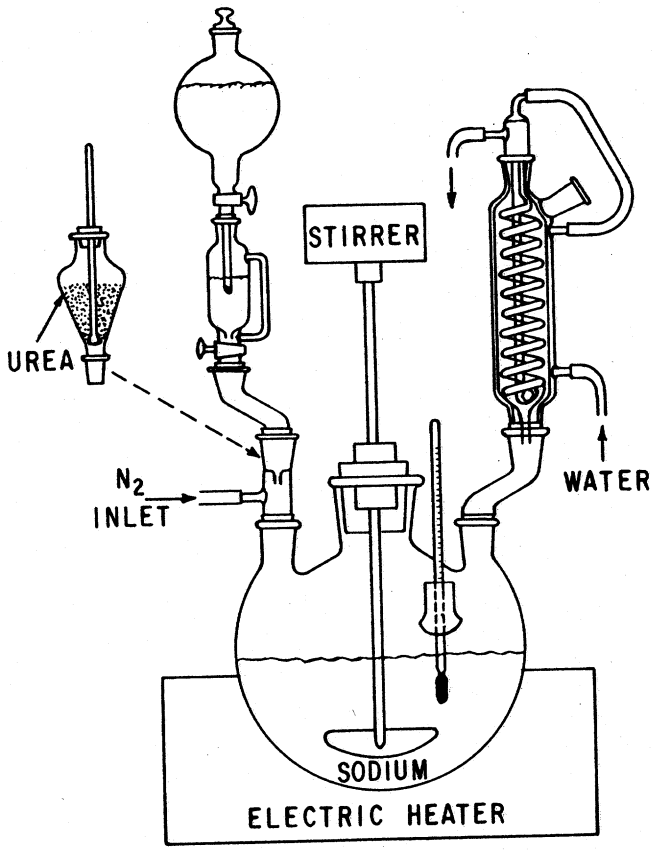

FIG. 1. Equipment used for reductions.

stirrer, large capacity condenser, and funnel arrangement for controlled, continuous liquid feed. For the decomposition step, the latter is replaced by the solid addition funnel set-up shown on the left. The flow of nitrogen in the tube below this addition funnel minimizes the wetting of descending solids by refluxing solvent vapors, and any plug-ups that still occur usually can be cleared by abrupt changes in nitrogen flow rate.

Preparation of Lard Oil Alcohols

Into a 3-L flask, equipped as shown in Figure 1, was introduced well cleaned sodium (125.7 g, 5.47 mole) and 400 ml xylene. The mixture was heated under nitrogen, and the molten sodium was finely dispersed by stirring. Lard oil (400 g, 1.37 equiv. of ester) and MIBC (277.0 g, 2.71 mole) dissolved in 500 ml xylene were added dropwise over a 2.5 hr period. The addition was made at such a rate as to minimize an undesirable molecular hydrogen generation and to help maintain the reaction mixture refluxing at 138 ± 2 C. A total of 263 ml xylene used for repeated rinses of the addition funnels then was added, and reflux of the stirred reaction mixture was continued until no more suspended sodium was visible (ca. 1.5 hr). After all the sodium had reacted, urea (328.0 g, 5.47 mole) was added to the stirred, refluxing reaction mixture over a period of ca. 20 min. The resulting viscous, pinkish-white reaction mass gradually became more mobile as the alcohols were liberated on decomposition of the sodium alkoxides. Stirring at reflux was continued until moist pH paper held at the condenser outlet indicated cessation of ammonia evolution (ca. 8 hr).

The final milky suspension was allowed to settle and cool to ~ 120 C, and then the resulting yellow supernatant was siphoned off and filtered. The residual solids (mostly sodium cyanate) were extracted repeatedly in situ until colorless, with 500 ml portions of xylene/MIBC (3:1) were filtered and combined with the filtrate from the supernatant. The total organic filtrate then was washed with 6 (300 ml) portions of water (the last of which was neutral) and dried over sodium sulfate. The xylene and MIBC were removed by continuous feed vacuum distillation from 70-140 C at ~ 3 torr. The residue (323.4 g) contained 91.1% fatty alcohols, 7.8% wax esters, and 1.1% fatty acids (determined by GC, TLC, and chemical analysis). HCl acidification of the cloudy, combined aqueous washes resulted in separation of an organic layer, that was removed. The remaining aqueous layer was extracted with 3 (200 ml) portions of CH_2Cl_2 and set aside for recovery of glycerol. The extracts were combined with the organic layer from the acidification, washed, dried, and freed of solvents. The residue (41.0 g) was comprised of 48.6% fatty acids 6.8% wax esters and 44.6% fatty alcohols (by chemical analysis). Neither of the products contained any triglycerides. The total yield of alcohols, including those contained in the 28 g, 7.3% wax esters, was 90.0%. The free fatty acids (6.5%) in the reduction product were utilized in the subsequent esterification step. The dried white NaOCN cake weighed 356.0 g.

Preparation of Other Fatty Alcohols

The reduction of tallow oil gave an estimated 93% yield of alcohols, that of crambe oil gave 85.4% of alcohols (including those contained in the 31.1 g, 16.7% wax esters), and 6.8% free fatty acids (acid number). The reduction of oil mix A yielded 90.5% alcohols, including alcohols contained in the wax esters, and ~7.5% free fatty acids (by GC, TLC, and chemical analyses).

Preparation of Oleyl Alcohol

Crude oleic acid (Groco 5-L) was esterified in xylene using slight excess of MIBC in a reaction catalyzed by 2%/wt of p-toluene sulfonic acid. The reaction was driven to completion by azeotropic removal of water. The mixture was allowed to cool and was filtered to remove the catalyst. The resulting MIBC-oleate, without isolation, was reduced as above to yield oleyl alcohol.

Preparation of Lard Oil Acids

Lard oil (350.0 g, 1.20 equiv. of ester) along with 875 ml methanol and 11 ml water was added to a stirred solution of NaOH (58.6 g, 1.46 mole) in 590 ml methanol, and the stirred mixture was refluxed for 5 hr under a stream of nitrogen. The mixture then was diluted with 1600 ml water, acidified with 10% H_2SO_4, and further diluted with 800 ml water. Upon cooling, the separated aqueous layer was drawn-off and extracted with 3 (400 ml) portions of CH_2Cl_2. These extracts then were added to the organic acid layer, and the resulting solution was washed with 3 (80 ml) portions of water. The organic layer was freed of solvent on a rotary vacuum evaporator to give 335 g acids (theory = 335 g).

Preparation of Other Fatty Acids

The fatty acids of crambe oil, oil mix A and tallow oil were obtained in identical fashion and in similar yields.

Synthesis of Lard Oil Wax Esters

A mixture of lard oil reduction products (351.6 g) composed of alcohols (301.5 g, 1.136 mole), wax esters (27.0 g, 0.0513 mole), and acids (23.1 g, 0.0828 mole) was dissolved in 500 ml toluene. This solution then was combined with 700 ml toluene containing lard oil fatty acids (296.0 g, 1.06 mole) and p-toluene sulfonic acid monohydrate (6.38 g, 0.0332 mole) equal to 2%/wt of the total fatty acids present. The mixture, with N_2 bubbling into it, was heated to and maintained at reflux until the

TABLE I

Composition Data on Wax Ester Products

Starting material	Wax ester (fraction)	Iodine value	Acid no.	Saponification no.
Oleic acid (Groco 5-L[a]	Total	94.0	0.7	106.4
Crambe oil	Total	100.4	0	93.8
Tallow oil	Liquid[b] (79%)	74.5	11.4	—
Oil mix A	Liquid[b] (76%)	78.6	0.9	105.1
	Solid (24%)	43.3	—	—
	Total	70.2	1.0	110.7
Oil mix A	Liquid[c] (97%)	72.2	1.1	111.7
	Solid[d] (3%)	20.7	1.0	111.9
	Total	82.5	—	110.2
Lard oil	Liquid (94.4%)	83.5	2.1	108.5
	Solid (5.6%)	27.9	—	—
Oleic acid	Total[d]	88.7	9.1	108.3

[a]Methyl isobutylcarbinol-esters formed in toluene and isolated.

[b]Winterized at 8 C (48 hr.).

[c]Filtered and pressed at room temperature.

[d]Methyl isobutylcarbinol-esters formed in xylene and reduced without isolation.

21.1 g) was azeotropically removed (~ 4 hr), thus driving the esterification to completion. After cooling, the mixture was transferred to a separatory funnel and washed with 7 (400 ml) portions of water, the last of which was neutral. The product solution then was stripped of solvent by vacuum distillation to 140 C at 2.3 torr. The residue (631.0 g) had a sap. no. of 110.7, IV of 82.5, and 98% wax ester content by GLC and TLC. Based upon the 708 g lard oil used, theory calls for (638.5 g); therefore, recovery = 98.8%, and overall conversion to wax esters = 96.8%.

Preparation of Other Wax Esters

Products from the reduction of crambe oil, tallow oil, and oil mix A were caused to react in a similar fashion with fatty acids obtained from the corresponding oils, and similar yields of wax esters resulted. The reduction products from the MIBC-esters of (Groco 5-L) oleic acid were caused to react with oleic acid to obtain oleyl oleate.

Winterization

The oleyl oleate wax esters remained liquid at 8 C, but oil mix A and tallow oil wax esters became slushy solids at the same temperature. To make these wax esters comparable to winterized sperm whale oil, the following treatment was applied to them: a batch of tallow oil wax esters (361.2 g) was cooled for 48 hr at 8 C. The resulting slush was filtered at 8 C in vacuo with pressing in small portions through an (M) sintered glass funnel at the same temperature. The pressed portions were recombined and again filtered with pressing. The resultant pressed cake (76.1 g) comprised 21% of material winterized and the filtrate (285 g) 79%. Other batches of oil mix A and lard oil, which after several months at room temperature showed some solids, were suction filtered with pressing at 27 C. These filtrations resulted in 94.4% liquid and 5.6% solid fractions from lard oil wax esters, while oil mix A wax esters gave 97% liquid and 3% solid fractions.

RESULTS AND DISCUSSION

Product compositions of wax esters prepared are listed in Table I. Evaluation of lubricant properties of some of these products and their derivatives will be reported elsewhere (H.E. Kenney, A. Eisner, T. Perlstein, E.T. Donahue, and I. Schmeltz, unpublished results).

The Bouveault-Blanc reduction of esters to sodium alkoxides is believed to proceed through a series of five reaction steps, as detailed by Hansley (1). This rationalization explains the need for a ratio of 4 moles of sodium and 2 moles of reducing alcohol/equivalent of ester to be reduced. In practice, a 5% excess of these reactants usually is employed to ensure complete reduction. Hansley also explains that the use of a lower ratio of reactants results in the formation of condensation products, such as acyloins. Adequate agitation and a sufficiently high reaction temperature to prevent gel formation help to avoid by-product formation by keeping the reaction mixture fluid and thus permitting the unreacted ester and its intermediates effective contact with surfaces of sodium globules. The choice of xylene as solvent and MIBC as reducing alcohol permits reflux at a satisfactory reaction temperature (138 ± 2 C).

Use of MIBC as reducing alcohol has several advantages. The sodium salt of MIBC is more soluble in refluxing xylene than most other alkoxides, and this solubility aids in keeping the reaction mixture fluid. Furthermore, this secondary alcohol has an optimum reaction rate for minimizing the formation of free hydrogen. The latter, according to Hansley, is not utilizable in the Bouveault-Blanc type reduction. The slow addition of the xylene solution of esters and reducing alcohol to the sodium disperison also aids in preventing molecular hydrogen formation.

The reaction mixture was kept under flowing nitrogen to maintain anhydrous conditions during reduction, and thus to minimize the fire hazard. The use of urea for the in situ decomposition of the sodium alkoxides, instead of water (2,3), is convenient and also serves to alleviate the fire hazard.

Oils suitable for Bouveault-Blanc reduction should be low in free fatty acids to minimize emulsion formation during isolation steps. For the same reason the use of well cleaned sodium is recommended.

The initial triglyceride mixture used, oil mix A, was so blended as to lead to a wax ester mixture similar to that found in natural sperm whale oil. The wax esters so prepared from oil mix A indeed approximated the chain length distribution of those found in the natural material, when compared by GLC. However, the degree of unsaturation of the oil mix A derivatives was somewhat lower than that of the wax esters in sperm whale oil. Table II compares oil mix A wax esters and its fractions from winterization with those from sperm whale oil (5).

Oleic acid (Groco 5-L) was esterified both to the methyl and MIBC esters. Both esters, dissolved in xylene, were reduced with sodium in the usual manner. The MIBC ester required less xylene to maintain fluidity, and the better contact of ester and intermediates with sodium resulted in greater sodium reduction efficiency, easier isolation and higher yield of oleyl alcohol when the MIBC ester was used. In the latter case alcohol recovery also was simplified, since decomposition of its reduction product liberated the same

TABLE II

Analyses of Oil Mix A and Sperm Whale Oil Wax Esters

	Oil mix A wax esters			Sperm whale oil wax esters[a]	
	Area % by gas liquid chromatography			Area (%)	Area (%)
Carbon no.	Liquid	Solid	Total	Total oil	Wax ester
<24	7.6	2.5	5.2		
24	2.1	1.8	3.0	Trace	Trace
25	Trace	Trace	Trace		
26	3.7	4.4	3.9	1.1	1.3
27	0.1	0.2	0.1	0.1	0.1
28	3.9	11.8	5.8	3.3	3.8
29	0.1	0.2	0.1	0.6	0.7
30	12.8	13.1	12.7	8.2	9.6
31	0.2	0.3	0.2	1.1	1.3
32	6.9	13.2	8.8	16.0	18.7
33	0.3	0.5	0.3	2.4	2.8
34	19.5	17.9	18.5	24.0	28.0
35	0.7	0.8	0.7	2.9	3.4
36	26.9	17.0	25.5	17.0	19.8
37	0.8	?	?	0.3	0.4
38	3.6	8.1	5.0	6.8	7.9
39	0.2	0.2	0.2	Trace	Trace
40	8.1	6.3	8.2	1.8	2.1
41	0.2	Trace	—	—	—
42	0.5	0.7	0.7	0.1	0.1
43		—	—		
44	0.6	0.6	0.7		
>44	0.4	0.2	0.4		
	99.2	99.8	100.0	85.7	100.1

[a]Analysis of sperm whale oil wax esters, ref. 5.

alcohol as the salt of the reducing alcohol.

It became evident in the initial reductions of oil mix A, that some wax esters were being formed directly as by-products (over 15%). The formation of these by-products suggested the idea of so altering reaction parameters as to promote wax ester formation to the point where it became the principal reaction. Initial probe runs, in which lower ratios of reactants and variations in reaction conditions were resorted to, did not prove fruitful.

In the next series of experiments, the MIBC-ester of stearic acid was used as model starting compound and the reaction sequence was mofified. Reduction of the ester was followed by addition of a second equivalent of ester rather than by decomposition of the sodium alkoxides formed. This new mixture then was refluxed for 4 hr. After urea decomposition, the isolated products contained mainly octadecanol and minor amounts of MIBC-stearate, stearyl-stearate, and polar material. The outsized cake left proved to be a mixture of sodium cyanate and stearamide. The latter was formed presumably by ammonolysis of ester by ammonia released during the urea decomposition.

Repetition of the described reaction sequence on lard oil resulted in similar final products, but the reduction mixture turned red, and very heavy foaming occurred during addition of second portion of lard oil. A sample of this foam proved to contain ca. 40% MIBC-esters, 30% wax esters, and 30% lard oil alcohols. Aliquots taken at 2 hr intervals after the second lard oil addition contained mainly alcohols and polar material. Glycerides were essentially absent. After decomposition with urea and work-up as before, the product contained mainly fatty alcohols, and the cake was composed of NaOCN and fatty amides.

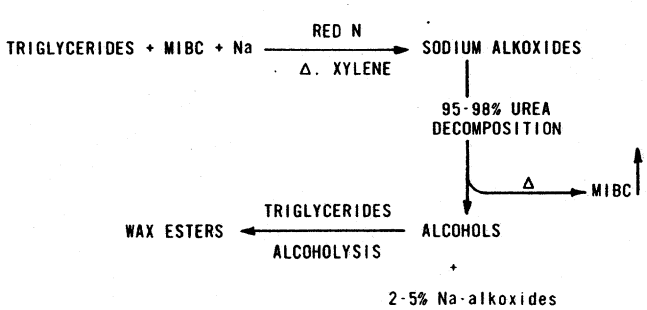

FIG. 2. Successful reaction sequence. MIBC = methyl isobutyl carbinol.

The next modification, also carried out on lard oil, involved partial decomposition of the ester reduced initially. The amount of urea added was limited to retain 10% of the sodium alkoxides as catalyst for the subsequent transesterification. The second portion of lard oil then was added, and the mixture was refluxed for several hours. Work-up of this reaction mixture yielded a product composed of ca. 30% lard oil alcohols, 30% MIBC esters, and 40% wax esters. These results, while promising and the best to this point, also pointed up the fact that competition from MIBC in the mixture with the lard oil alcohols would preclude any further significant increase in the formation of lard oil wax esters. To eliminate this limiting factor, it was necessary to remove the MIBC liberated during the decomposition and thus to prevent its competition in the alcoholysis to wax esters.

In the third experiment, therefore, the reduction of the lard oil was affected in the usual manner; and, while 95% of the resulting alkoxides was being decomposed, the MIBC liberated was removed by azeotropic distillation with xylene. Replenishment of the reaction mass with fresh xylene was continued until distillate fractions were free of MIBC and ammonia evolution had ceased. A second portion of lard oil then was added, and the mixture was stirred at reflux for 4 hr. An aliquot taken only 5 min after second lard oil addition showed complete disappearance of triglyceride by TLC, and the 2 and 4 hr aliquots contained 80 to 90% wax esters after work-up. The successful reaction sequence is diagrammed in Figure 2.

In confirming experiments on both lard oil and tallow oil, the reproducibility of these results was demonstrated. Furthermore, it was shown that the alkoxides required as transesterification catalysts can be the result of partial urea decomposition of the reduction products or can be added to the alcohol mixture subsequently.

The Bouveault-Blanc reduction and urea decomposition route was employed in preparatory scale runs and resulted

in 90% or higher yield of alcohols and in overall conversion to wax esters in excess of 95%. However, this route involves three reaction sequences with three separate product isolations.

The more direct route to wax esters results in only 80-90% conversion to wax esters based upon total triglycerides used, but it has fewer steps and requires only one isolation. This isolation is made with xylene only to avoid further alcoholysis. However, the final product contains some fatty alcohols from the decomposition of the alkoxides used as catalyst. The fewer steps, and the less equipment and handling required in this more direct route, should make this process more advantageous on a large scale. Furthermore, the reactant costs/lb wax ester produced in the second, more direct process is only ca. 80-90% of the costs in the first process. The potential value of concurrently formed NaOCN and glycerol by-products possibly could reduce costs of both routes significantly.

ACKNOWLEDGMENTS

Oil mix A gas liquid chromatographic analysis (Table II) was performed by G.F. Spencer, Industrial Crops Laboratory, Northern Regional Research Center, USDA, Peoria, Ill. Assistance in analyses and in experimental work was provided by D. Lentz, P. Heller, and T. Barber.

REFERENCES

1. Hansley, V.L., Ind. Eng. Chem. 39:55 (1947).
2. Kamlet, J., U.S. Patent 2,563,044 (1951).
3. Barrett, F.O., Fitzpatrick, J.D., and Kadesch, R.G., Ind. Eng. Chem. 45:1114 (1953).
4. Luddy, F.E., J.W. Hampson, S.F. Herb, and H.L. Rothbart, JAOCS 50:240 (1973).
5. Spencer, G.F., and W.H. Tallent, JAOCS 50:202 (1973).

[Received April 22, 1974]