Summary

Tests conducted on a pilot-plant scale with two lots of commercial, alkali-refined safflower oil demonstrate that no difficulty is experienced in producing a salad oil of good, initial quality with good flavor stability when stored at 60°C. in the dark. Although results indicate safflower oil is suitable for a salad oil, they should not be construed as indicating its stability as a cooking oil since tests of this type were not conducted.

The addition of citric acid improved the oxidative stability of the oil, and citric acid plus propyl gallate gave even further improvement. No significant increase in flavor stability resulted from these additives.

Acknowledgments

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The Preparation and Infrared Spectra of Morpholides of Ricinoleic Acid and Some of Its Derivatives

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PREPARATION of the morpholides of ricinoleic acid and some of its derivatives was undertaken as part of a research program on the chemistry of castor oil. Ricinoleic acid, 12-hydroxyoleic acid, comprises about 90% of commercial castor oil. Morpholides have generally been prepared by the reaction of morpholine with acid chlorides, acids, or acid anhydrides (1–6). There appear to be only two references in the literature to the preparation of morpholides by the action of morpholine on esters and none on the reaction of morpholine with esters of long-chain fatty acids. Ratchford and Fisher (7) in a study of the preparation of N-substituted lactamides by ammonolysis of methyl lactate report a yield of 83% of the morpholide without giving experimental details. Utermohlen (8) in a patent on a process for acylating amines reported that refluxing isopropenyl acetate with morpholine in the presence of sulfuric acid as a catalyst produced N-acetylmorpholine.

Because the ammonolysis of esters is a well-recognized reaction, the preparation of the morpholides of ricinoleic acid and some of its closely related derivatives by reaction of morpholine with the methyl esters was investigated. It was found that although the reaction is rather slow, the morpholides could be obtained in substantially quantitative yield simply by refluxing the methyl esters with an excess of morpholine and condensing the evolved methanol in a Dean-Stark trap. Since the distillation temperature of methanol (65°C.) is quite different from that of morpholine (129°C.), efficient fractionation is not required and relatively little of the excess morpholine distills over with the methanol. The progress of the reaction could be followed roughly by observing the rise in refluxing temperature and more accurately by titrating the unreacted morpholine, using mixed methyl red and methylene blue indicator (9). The morpholide of stearic acid, which does not seem to have been reported previously, was prepared for purposes of comparison.

The infrared spectra of the morpholides showed characteristic absorption bands which can be used for diagnostic purposes and for analysis. A strong band at 5.78 microns is characteristic of the esters. An equally strong band at about 6.10 microns present in all the morpholides, completely separated from the 5.78 micron band and absent from the spectrum of morpholine, characterizes the morpholides.

The morpholides, but not morpholine, also exhibit a band of moderate intensity at about 10.3 microns. Hence the morpholides represent another class of compounds in which *trans* unsaturation cannot be detected by use of this band (10).

Experimental

Materials. Methyl ricinoleate was prepared from the oil by the method of Swern and Jordan (11). The methyl ricinoleate used typically had the following characteristics: N_D^{20} 1.4629; d_{25}^{25} 0.9233; $[\alpha]_D + 5.004$, all in good agreement with the reported values. The hydroxyl content was 5.43% (theory 5.45%).

Methyl ricinelaidate was prepared from methyl ricinoleate by elaidinization with sulfur according to the method of Rankov and Iochev (12). Repeated crystallization from Skelly F[2] gave a product of constant melting point, 27.5–28.0°C.

Since the preparation of the morpholides was, in general, quite similar, only the preparation of 4-ricinoleoylmorpholine will be described.

To a one-liter flask provided with a short Vigreaux column, reflux condenser, Dean-Stark trap and thermometers to measure the temperature of the liquid and vapor were added 312 g. of methyl ricinoleate (1 mole) and 174 g. of morpholine (2 moles). The reaction mixture was heated at gentle reflux for about 36 hrs., during which time the reaction temperature gradually rose from 145 to 180°C. and approximately one mole of methanol was evolved. The vapor temperature at the Dean-Stark trap was generally well below 75°C. The course of the reaction could be conveniently followed by titrating one-milliliter aliquots for unreacted morpholine from time to time. When the reaction was completed, the excess morpholine was removed under reduced pressure and the reaction product was dis-

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[2] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

TABLE I

Absorption Bands in the Infrared Spectra of Morpholine and Morpholides from Ricinoleic Acid Derivatives

Curve—functional group	Wavelength position (microns) of maxima						
	A	B	C	D	E	F	G
1. O—H stretching	......	2.78	......	......	2.82	......	2.82
2. Unassigned	2.90	2.88	2.91	......	2.90	2.90	2.89
3. N—H stretching	......	......	......	2.97 and 3.09	......	......	......
4. C—H stretching	3.44	3.43	3.44	3.42	3.45	3.42	3.42
5. C—H stretching	3.49	3.49	3.49	3.51 and 3.69	3.49	3.49	3.49
6. Unassigned	......	......	......	4.00 and 5.19	......	......	......
7. C=O stretching (ester)	......	......	5.78	......	......	5.78	......
8. C=O stretching (amide)	6.08–14	6.07–11	6.10-12	......	6.12	6.08–16	6.06–12
9. C—H deformation (—CH$_2$, —CH$_3$)	6.84	6.83	6.83	6.86	6.84	6.83	6.82
10. C—H deformation	6.97	6.94	6.99	6.92	6.93–4	6.98	6.95
11. C—H deformation	7.33	7.32	7.27	7.25	7.33	7.26	7.32
12. Unassigned	......	......	......	7.40 and 7.58	......	......	......
13. C—N	7.68	7.68	7.68	7.65	7.68	7.68	7.66
14. C—O stretching	7.89	7.87–90	7.93	7.85	7.87	7.92–99	7.85
15. Unassigned	8.96	8.96	8.96	8.80 and 9.05–10	8.96	8.96	8.94
16. O—O, C—N stretching	9.35	9.36	9.36	9.44	9.36	9.35	9.34
17. Unassigned	9.75	9.80	9.80	9.73 and 9.88	9.73	9.79	9.70
18. Unassigned	10.36	10.36	10.38	......	10.35	10.36	10.25
19. Unassigned	10.98	11.00	10.98	11.04 and 11.25	11.00	......	10.96
20. Unassigned	11.79–83	11.82	11.82	11.95–9	11.79	11.82	11.80

A = 4-stearoylmorpholine, B = 4-(12-hydroxystearoyl)morpholine, C = 4-(12-acetoxystearoyl)morpholine, D = morpholine, E = 4-ricinoleoylmorpholine, F = 4-(12-acetoxyoleoyl)morpholine, G = 4-ricinelaidoylmorpholine.

tilled. Distillation gave 320 g. of material distilling at 243–246°C. at 0.2 mm.; N_D^{25} 1.4891; d_{25}^{25} 0.9756 $[\alpha]_D$ 4.27. Anal. Calcd. for $C_{22}H_{41}O_3N$ (367.6): C, 71.88; H, 11.24; N, 3.81; OH, 4.63. Found: C, 71.47; H, 11.02; N, 3.80; OH, 4.68.

When methyl 12-hydroxystearate was used, 330 g. of distillate boiling at 245–249°C. at 0.25 mm. and melting at 46.5–48.5°C. were obtained. Repeated crystallization from Skelly B[2] gave a product of constant melting point, 52.5–53°C. Anal. Calcd. for $C_{22}H_{43}O_3N$ (369.6): C, 71.49; H, 11.73; N, 3.79; OH, 4.60. Found: C, 71.53; H, 11.79; N, 3.75; OH, 4.59.

The morpholide of ricinelaidic acid prepared from methyl ricinelaidate distilled at 209°C. at 0.1 mm. and melted at 26.2–26.8°C. Anal. Calcd. for $C_{22}H_{41}O_3N$ (367.6): C, 71.88; H, 11.24; N, 3.81. Found: C, 71.23; H, 11.27; N, 3.90.

The morpholide of stearic acid prepared from purified methyl stearate, m.p. 39.2–40°C. after recrystallization from methanol (5 ml. per gram and 10 ml. per gram) and then from Skelly B[2] (25 ml. per gram) gave a constant melting point of 52.3–52.8°C. Anal. Calcd. for $C_{22}H_{43}O_2N$ (353.6); C, 74.73; H, 12.26; N. 3.96. Found: C, 74.81; H, 12.16; N, 3.87.

The acetoxy derivatives were prepared by refluxing the morpholides of ricinoleic acid and of 12-hydroxystearic acid with an equal weight of acetic anhydride for two hours, removing the acetic acid and excess acetic anhydride at slightly reduced pressure, and then distilling acetylated product at greatly reduced pressure. The 4-(12-acetoxyoleoyl)morpholine distilled at 230–234°C. at 0.2 mm.; N_D^{25} 1.4789; d_{25}^{25} 0.9836; $[\alpha]_D$ 20.35. Anal. Calcd. for $C_{24}H_{43}O_4N$ (409.6): C, 70.37; H, 10.58; N, 3.42; OH, 0. Found: C, 69.99; H, 10.53; N, 3.24; OH, 0.

The 4-(12-acetoxystearoyl)morpholine distilled at 234–235°C. at 0.2 mm.; N_D^{25} 1.4709; d_{25}^{25} 0.9726; $[\alpha]_D$ 0.09. Anal. Calcd. for $C_{24}H_{45}O_4N$ (411.6); C, 70.03; H, 11.02; N, 3.40; OH, 0. Found: C, 69.62; H, 11.17; N, 3.24; OH, 0.

Infrared absorption curves were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer.[2] The settings used were: resolution, 927; suppression, 3; gain, 6; response, 1; and speed, 4. All spectra were obtained as chloroform solutions at concentrations of about 40 g. per liter with an absorption cell 0.51-mm. in path length. Pure dry chloroform was placed in the reference beam; absorption of chloroform was completely eliminated from the resulting spectra by this differential technique. The wavelength positions of absorption maxima for all absorption bands in these spectra with absorptivities of *ca.* 0.5 or greater are compared in Table I.

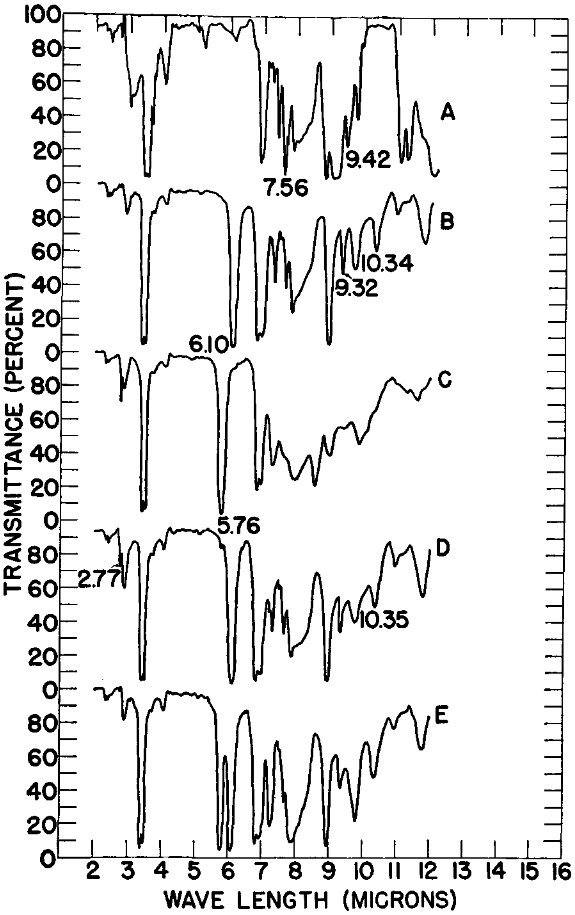

FIG. 1. Infrared spectra of morpholine and saturated derivatives of ricinoleic acid.

A = morpholine, B = 4-stearoylmorpholine, C = methyl 12-hydroxystearate, D = 4-(12-hydroxystearoyl)morpholine, E = 4-(12-acetoxystearoyl) morpholine.

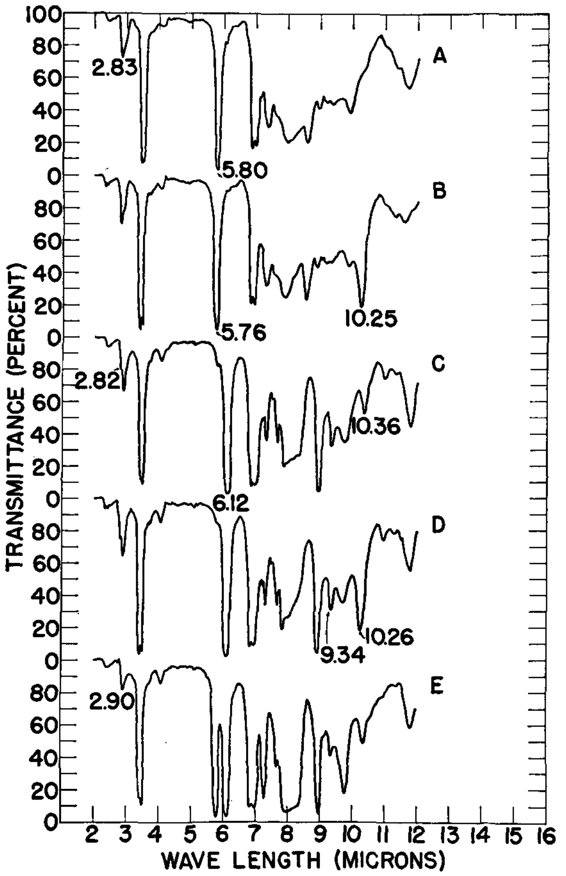

Fig. 2. Infrared spectra of unsaturated derivatives of ricinoleic acid.
A = methyl ricinoleate, B = methyl ricinelaidate, C = 4-ricinoleoylmorpholine, D = 4-ricinelaidoylmorpholine, E = 4-(12-acetoxyoleoyl)morpholine.

Discussion of Infrared Spectra. In the region of O–H and N–H stretching below 3.0 microns a band at 2.90 μ appears to be characteristic of the morpholide moiety (Figure 1 B, D, and E and Figure 2 C, D, and E). However as a weaker band, at somewhat shorter wavelength, is characteristic of the hydroxy esters (Figure 1 C and Figure 2 A and B), this band would not be of any diagnostic value. The bands at 2.97 and 3.09 microns, which arise from N–H stretchings, are observed only in the spectra of the unreacted morpholine. These bands could probably be used to detect or measure any unreacted morpholine. Their weak intensities would limit the sensitivity for the detection of morpholine.

The C–H stretching vibrations at about 3.4 and 3.5 microns and the C–H deformations at 6.8, 6.9, and 7.3 microns are noteworthy mostly for their similarity in the spectra of all reactants and reaction products. The spectrum of morpholine (Figure 1 A) alone exhibits characteristic bands at 4.00, 5.19, 7.40, and 7.58 microns for which no correlations have been offered (13). Any of these four bands should permit the detection and measurement of unreacted morpholine. The band with maximum at 7.58 microns has proven to be the best suited for this purpose in the few tests made in this laboratory.

The strong bands in the region of 5.7 to 6.2 microns are probably of greatest importance. The band with maximum at about 5.78 microns arises from the C=O stretching of the ester group (14) and is observed only in the spectra of the compounds containing this group (Figure 1 C and E and Figure 2 A, B, and E). At about 6.10 microns a second strong band, completely resolved from the 5.78-micron band in the spectra in which both appear, arises undoubtedly from the morpholide moiety. It is found in the spectra of all the morpholides but not in that of any of the reactants including morpholine itself. This strong band which appears in the spectra of all amides (15), arises undoubtedly from a C=O stretching of the substituted amide group. The band at 5.78 microns can be used as a relatively sensitive test for unreacted ester. The band at 6.1 microns likewise can be used to detect the formation of the morpholide reaction product, to measure its concentration, or to follow the kinetics of the reaction. A band with maximum at 7.68 microns is found in the spectra of morpholine and all the morpholides. According to Colthup (16), amines of various types have infrared group absorption in this region, and most of these probably involve C–N stretching vibrations.

A band at 7.9 microns commonly recognized in esters as caused by a C–O stretching (14) appears in the spectra of all these compounds, including morpholine, and may be assigned to a C–O stretching of the morpholine moiety. The band at 9.36 microns (9.44 microns in the spectrum of morpholine) is observed only in the spectra of the compounds containing the morpholide ring and may arise from a stretching of the C–O or the C–N group.

Above about 9.0 microns it becomes increasingly difficult to assign a specific vibrating group to account for each absorption band. The specific bands in the region between 9 and 12 microns can be used in a fingerprint comparison to identify or distinguish these compounds. It is of interest to note that the morpholides, but not morpholine, exhibit a band of moderate intensity at about 10.3 microns. The wavelength position is usually attributed to a C–H bending about an isolated *trans* double bond. In the spectrum of methyl ricinelaidate (Figure 2 B) the band with maximum at 10.25 microns can be attributed to this deformation. It is not observed in the spectrum of methyl ricinoleate (Figure 2 A). In the spectrum of 4-ricinoleoylmorpholine (Figure 2 C) the band at 10.35 microns, like that exhibited by all morpholides, must be attributed to a vibration of this moiety. The spectrum of 4-ricinelaidoylmorpholine (Figure 2 D) exhibits a much stronger and somewhat broader band at 10.25 microns, undoubtedly arising from both a vibration of the morpholide moiety and the C–H bending about *trans* C=C. Morpholides therefore represent still another group of compounds in which *trans* unsaturation cannot be detected by use of this band (10, 17).

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Error in the Sampling of Soap and Detergent Bars for Moisture Determination

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INSTRUCTIONS of the American Society for Testing Materials for the sampling of soap and combination bars specify passing the entire bar through a suitable chopper or, when this is impossible because of the nature of the sample, that a cake be quartered by cutting at right angles in the center and sufficient sample obtained for analysis by shaving equally from all freshly cut surfaces (1).

Sampling by the latter alternative is widely practiced in preference to the chopper method, which is messy and time-consuming. It is based on the assumption that the moisture content of longitudinal slices from the center of a bar approximate the average moisture content of the bar as a whole and that dehydration of the corners of the bar does not affect significantly the average moisture content.

The A.O.C.S. directions for the sampling of bar soap are more precise. They specify grinding of the entire bar or, in the case of large samples, permit quartering of the bars and grinding quarters from each bar. It is further specified that each ground sample should consist of at least three pounds before subsequent reduction to a laboratory-size sample by successive quartering (2).

Griffin (3) gives a further variation for sampling, recommending the grinding of whole bars or, alternately, cutting each cake diagonally and shaving from the freshly cut surfaces.

A study of the moisture level in all parts of a single bar indicates that an appreciable error may arise in sampling for moisture content unless the whole bar or a symmetric portion thereof, such as a half or full quarter of the bar, is taken for analysis.

The magnitude of the error may be evaluated by determining the moisture content of center slices *versus* the remainder of the full quarter of the bar. Table I gives results for a series of such comparative determinations.

A simple calculation based on the respective weights of sample taken for analysis of milled soap No. 2 (Table I, first week) indicates that if the whole bar were taken for analysis, the moisture content would be 9.49%, whereas the moisture value obtained by the taking of slices would indicate the moisture to be 10.01%. This difference is considerably greater than the experimental error of the determination, which in the case of bar soap is approximately ± 0.1%.

TABLE I
Moisture Content of Bars: Center Slices *vs.* Whole Quarter

Sample designation	Aging period before analysis	Moisture content (oven method)	
		Shaved slices	Remaining quarter
Milled soap No. 1	1st week	7.53	6.96
Milled soap No. 2	1st week	10.01	9.24
Milled soap No. 2	2nd week	8.84	8.55
Milled soap No. 2	3rd week	8.75	8.26
Milled soap No. 2	4th week	7.79	7.44

The results for soap No. 2 in Table I also show that, as the age of the soap increases, the difference in moisture content resulting from the two methods of sampling tends to diminish.

In view of the fact that the result for the determination of moisture in a bar product varies with the method of sampling, it was considered of sufficient interest to determine the moisture content of a bar simultaneously in as many areas as practical. Accordingly 24 samples were taken from one bar of milled toilet soap, and the moisture was determined on a semi-micro scale by the oven method at 105°C. The samples were taken by means of a thin cork borer, and each plug (surface to surface of the bar) weighed about 0.22 g. Figure 1 shows the points of sampling, and Table II gives the results for the moisture determination.

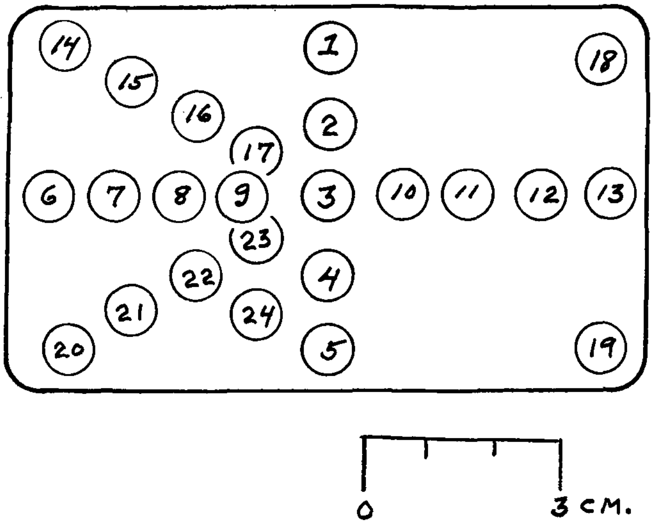

FIG. 1. Location of moisture-sampling sites in a single bar of soap.