pared from sesame oil was found to be 35.1%, which agrees reasonably well with the calculated value of 37.3%.

The method has been applied to the determination of free and bound sesamol in a number of samples of crude, refined, bleached, hydrogenated, and deodorized sesame oils as part of an investigation of the role played by sesamol in the stability of these oils.

Summary

The Villavecchia test was adapted for the quantitative determination of sesamol in sesame oil. Of the several aromatic aldehydes tested, furfural, in the presence of aqueous sulfuric acid (sp. gr. 1.37 at 15°C.), proved to be the most suitable for the quantitative measurement of the color produced with sesamol.

The oil, dissolved in iso-octane (10 g. per 100 ml.), is shaken with dilute aqueous-alcoholic potassium hydroxide to remove the free, but not the bound sesamol. The modified Villavecchia test is applied to a) the original iso-octane solution of the oil, b) the iso-octane solution after extraction with alkali, and/or c) the aqueous-alcoholic extract. The optical densities, read at a wavelength of 518 mμ, correspond to the total bound, and free sesamol, respectively.

The method was applied to the determination of free, bound, and total sesamol in a number of crude, refined, bleached, and deodorized sesame oils. Agreement between the values for total and free plus bound sesamol was close. Four crude sesame oils of different origins had total contents of sesamol ranging from 0.13 to 0.17%, of which nearly all was in the bound form. The yields of added sesamol varied from 95 to 106%.

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Molecularly Distilled Monoglycerides[1] I. Preparation and Properties[2]

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THE widespread use of monoglycerides has developed in the last decade although methods for preparing them have been known since the mid-19th century. In the presence of an alkaline catalyst, either direct esterification of fatty acids or interesterification of fats provides a convenient method for preparing monoglycerides. The reaction product is a mixture of monoesters, diesters, and triesters as well as free glycerol, free fatty acid, and the catalyst in the form of metallic soaps. The term monoglyceride has been loosely applied to this total reaction mixture in which the glyceryl monoester is frequently a minor constituent.

Up to the present there has been little or no concentration of monoester from such a mixture on a commercial basis. The wide range in molecular weights of the components of the mixture suggests a distillation process, but ordinary distillation is difficult because of the low vapor pressure and thermal instability of the monoester. Molecular distillation however is readily effective for separating the monoglyceride from the reaction mixture.

Molecular distillation is well-known and should not need any discussion in this paper. Essentially pure monoglycerides were obtained by molecular distillation of the reaction products of glycerol and a partially hydrogenated vegetable oil. A sample of one of the well-known products of the commercial monoglyceride mixture type was distilled on a 5-inch centrifugal molecular still (1).

Table I shows the temperature and pressure during the distillation of the monoglyceride mixture. Two small 5% cuts were taken to remove the low molecular weight components. Three 10% fractions, assaying over 90% monoester, were obtained from the original 41% monoglyceride mixture. The monoester was determined by the periodic acid oxidation method of Pohle, Mehlenbacher, and Cook (2) as modified by Handschumaker and Linteris (3).

The graph in Figure 1 shows the concentration of the various components. The bulk of the glycerol and fatty acids shown by the hatches is removed in the forepart of the distillation. The free fatty acids were determined by the A.O.C.S. procedure (4) and the glycerol by the method of Bradford, Pohle, Gunther, and Mehlenbacher (5). About 50% of the volatile glycerol escapes condensation on the condenser surface and is collected in the dry ice trap which is ahead of the pumping system. The major portion of the monoester is obtained in a substantially pure form and only small amounts of monoester are found in the di- and triglyceride fractions.

The above example is typical of the method used to prepare purified monoglyceride concentrates from a variety of oils and fatty acids. Data are presented

TABLE I

Operation Data for the Separation of Monoesters by Molecular Distillation of a Partially Hydrogenated Vegetable Oil Monoglyceride Mixture

Fraction	Temperature °C.	Pressure, mm. Hg.	% Cut	% Monoester
Charge	....	....	(100)	41
1	80-140	0.018	5.2	67
2	140-142	0.016	4.8	84
3	142-148	0.011	9.2	93
4	148-153	0.04	10.0	97
5	153-168	0.04	9.9	94
6	168-200	0.04	10.0	23
7	200-206	0.04	9.9	12
Residue	....	....	39.6	1

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[1] Presented at the 23rd Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 31, Nov. 1 and 2, 1949.

[2] Communication No. 165 from the Laboratories of Distillation Products Industries.

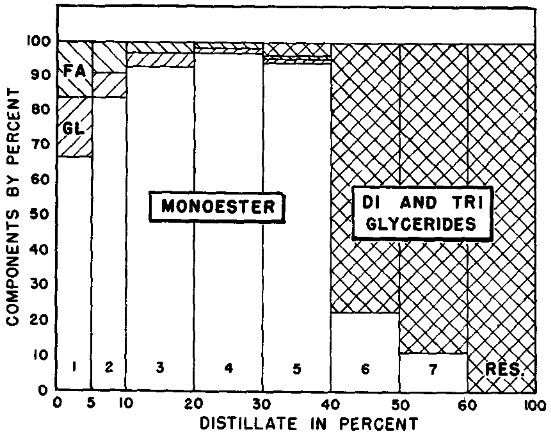

FIG. 1. Composition of the distillate from a molecular still distillation of partially hydrogenated vegetable oil monoglyceride reaction products. FA = free fatty acids; GL = free glycerol; RES = undistilled residue.

comparing the analyses of these distilled monoglycerides with those of commercial monoglyceride mixtures. The distilled monoester is usually paired with a corresponding commercial monoglyceride mixture. However in a few cases a commercial product was not available. Therefore those samples designated simply as laboratory mixtures were made in the laboratory under conditions approximating commercial methods.

TABLE II

Analytical Data on Products Containing Saturated Acid Monoesters of Glycerol

Monoglyceride Products	% Mono-ester	% Glyc-erol	% F.F.A.	Melting Point °C.	Color 5¼" Lovibond
Monolaurate					
Commercial Mixture	35	9.5	1.2	47	35Y/4.0R
Distilled Monoester	92	0.7	1.3	57	20Y/2.4R
Monopalmitate					
Laboratory Mixture	38	3.6	2.7	61	60Y/13.5R
Distilled Monoester	93	0	1.3	72	8Y/1.2R
Monostearate					
Commercial Mixture	40	3.9	2.3	59	12Y/1.9R
Distilled Monoester	94	0.5	1.2	71	10Y/1.5R

ANALYSES of monoglyceride products prepared from saturated acids are given in Table II. It will be immediately apparent that the monoester content of the distilled product is approximately twice that of the commercial mixture. The glycerol content of the distilled ester is frequently less than 1% whereas in most commercial mixtures the glycerol content is usually 3-4%. The free fatty acid content of monoglycerides prepared from fatty acids may vary from 1-10%. Distillation however permits a control of the fatty acid content. The melting point of the distilled monoester is invariably higher than that of the corresponding reaction mixture. The color of the monoesters made from saturated acids is usually good. However distillation improves the color.

In Table III analyses of several glyceryl monoesters of unsaturated acids are given. The monoester content of the distilled product is approximately twice that of the commercial mixtures. The glycerol and free fatty acid contents are considerably less in the distilled material.

The significant differences in melting points however may not have been expected. The increased melting point of the distilled monoesters, which is frequently 10-20°C. higher than that of the commercial mixtures, has a practical advantage when working with the unsaturated esters. For example, the monoester made from liquid cottonseed oil is a plastic product closely resembling a shortening in appearance.

The monoglyceride mixtures made from unsaturated fats frequently are exceedingly dark. Therefore the removal of the color bodies by distillation is much more marked when comparing the distilled and undistilled unsaturated monoglycerides. For example, the color of the distilled monoester of cottonseed oil is better than commercial saturated monoglycerides. Even products with as high a degree of unsaturation as soybean oil yield a distilled monoester which is almost water white. The monoester content and color are often the essential properties to be considered. For example, alkyd resins made from distilled soybean monoesters are practically colorless and have many other unusual properties associated with the monoglyceride purity.

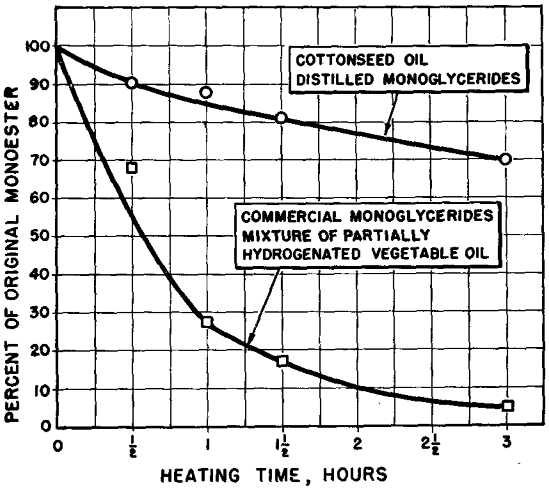

FIG. 2. The effect of heat (180°C.) upon the monoester content of monoglyceride products.

Saponification values and iodine values of the distilled monoester are always less than those of the reaction mixtures since these values will be decreased by the increased amount of combined glycerol. Odor and taste are also effectively removed by the molecular distillation process.

Products which are intended for edible use should be free of soap or other catalysts. It is difficult to remove the catalyst completely from a monoglyceride preparation by methods such as water washing or precipitation with phosphoric acid. Ash contents for commercial monoglyceride mixtures were found to be 820 p.p.m. of ash for a stearic acid product and 290 p.p.m. of ash for a partially hydrogenated vegetable oil product. The molecularly distilled monoglycerides however are substantially catalyst free with typical ash contents of 1 to 2 p.p.m.

PERHAPS the most important reason for catalyst removal is to minimize changes in monoester content. Figure 2 shows the monoester destruction when samples of a commercial monoglyceride mixture and a distilled monoglyceride are heated at 180°C. for a period of three hours. Most shortening manufacturers are aware of the monoglyceride loss encountered when the monoglyceride is added to shortening dur-

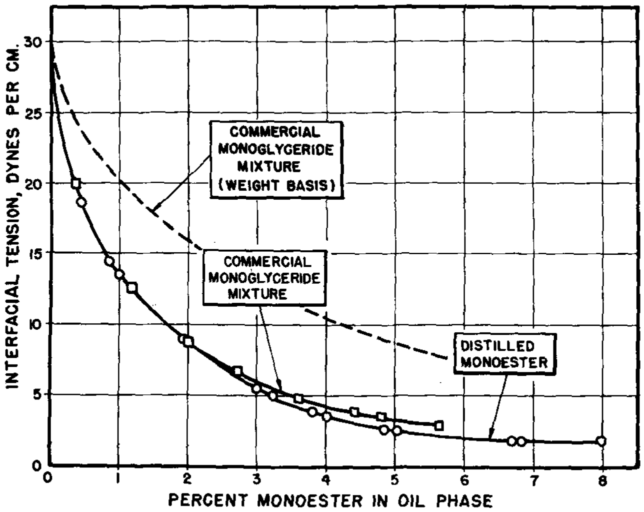

FIG. 3. Measurement of the reduction in interfacial tension between oil and water produced by various percentages of monoesters from triple-pressed stearic acid monoglyceride products.

ing the deodorization stage. Thus, even though the catalyst in the commercial reaction mixture has been partially removed, the residual catalyst is sufficient to promote the rapid destruction of the monoester.

Distillation has made it possible to obtain a reasonably pure glyceryl monoester. Subsequent studies were undertaken to determine the action of the monoester when free of the other components of the reaction mixture.

Monoglycerides are capable of lowering the interfacial tension of oil and water. Interfacial tension measurements have been made by the ring method using a Cenco-du Nöuy tensiometer. Correction values as determined by Harkins and Jordan (6) were applied to all readings. Each monoglyceride product was added at varying levels to a refined cottonseed oil and the interfacial tension of these mixtures was determined against water at 70°C.

The action of a commercial monostearate mixture containing 40% of the monoester and a distilled monostearate containing 94% of the monoester in lowering the interfacial tension is shown in Figure 3. Comparisons of commercial mixtures and distilled products in this discussion are based on the monoester content rather than on a weight basis. In comparing the distilled monoester and the reaction mixture on a weight basis, approximately 2.2 times more of the reaction mixture is used than of the distilled product. The action of a monoglyceride mixture when added on a weight basis is shown by the dotted line in the graph in Figure 3. The activity of the distilled monoglyceride plotted on a weight basis is essentially the same as that shown on a monoester basis. There seems to be little effect on interfacial tension due to the diester and minor constituents except at the higher level of monoester addition.

TABLE III

Analytical Data on Products Containing Unsaturated Acid Monoesters of Glycerol

Monoglyceride Products	% Monoester	% Glycerol	% F.F.A.	Melting Point °C.	Color 5¼" Lovibond
Monoesters, Part. Hyd. Veg. Oil					
Commercial Mixture	41	3.5	3.7	55	18Y/2.3R
Distilled Monoesters	95	1.0	1.0	54	8Y/1.2R
Monooleate					
Commercial Mixture	54	0.5	2.6	21	80Y/20R
Distilled Monoester	95	1.0	2.3	41	12Y/1.4R
Monoesters, Cottonseed Oil					
Laboratory Mixture	42	4.0	0.5	30	57Y/27R
Distilled Monoesters	93	2.0	0.5	51	8Y/1.2R
Monoesters, Soybean Oil					
Laboratory Mixture	49	2.5	0.7	18	155Y/16R
Distilled Monoesters	97	0	0.8	34	5Y/1.0R

Figure 4 shows the interfacial tension lowering obtained with a commercial monoglyceride mixture of a partially hydrogenated vegetable oil containing 41% of the monoester and the distilled product containing 95% of the monoester. Data points for these two products fall on the same curve indicating that the surface tension lowering is due solely to the monoester content.

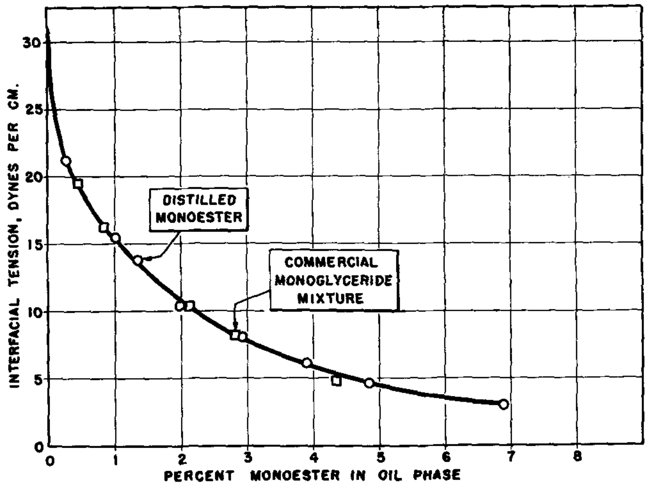

FIG. 4. Measurement of the reduction in interfacial tension between refined cottonseed oil and water produced by various percentages of monoesters from partially hydrogenated vegetable oil monoglyceride products.

The graph in Figure 5 compares a laboratory preparation of cottonseed oil monoglyceride reaction mixture containing 42% of the monoester with a corresponding 93% distilled monoester. There seems to be a small but measurable activity attributable to the other components of the reaction product. The interfacial tension lowering data obtained, using several distilled monoglycerides, are graphed in Figure 6.

If the saturated monoglycerides were plotted on a mole basis, the curves would practically coincide. In general, the saturated monoglycerides show a greater lowering effect than do the unsaturated monoglycerides, such as the cottonseed oil monoglycerides. This does not necessarily indicate that the saturated monoesters are much better emulsifiers than the unsaturated monoesters. A number of factors other than interfacial tension lowering also determine the practical efficiency of an emulsifier.

A simple water absorption test has been used to evaluate water-in-oil emulsifiers, such as monoglycerides. In this test the monoglyceride is added to a petrolatum base. Water is added to the oil phase in an electric mixer to form an emulsion (under carefully controlled conditions). The end point which occurs when the emulsion breaks, or no longer absorbs water, is usually characterized by a drop in the viscosity of the emulsion. This procedure is based on the method published by Griffin (7).

In Figure 7 the water absorption values are plotted

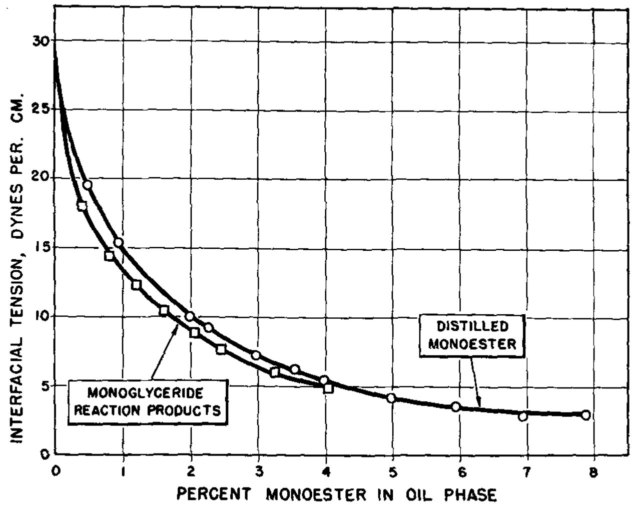

Fig. 5. Measurement of the reduction in interfacial tension between refined cottonseed oil and water produced by various percentages of monoesters from cottonseed oil monoglyceride products.

against the percentage of monoester in the oil phase. The distilled monoester made from triple-pressed stearic acid assaying 94% monoester is compared with the commercial monostearate mixture containing 40% monoester. It is evident that this glyceryl monoester has a greater emulsifying ability when the rest of the reaction mixture is absent. This type of test is probably closely associated with some conditions encountered in the cosmetic industry.

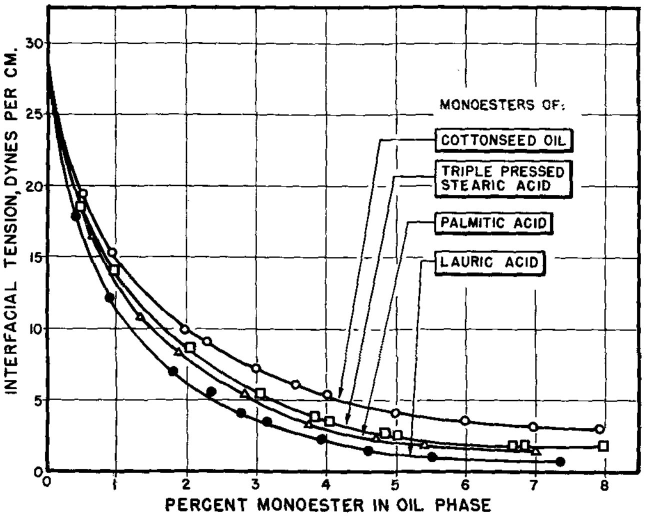

Fig. 6. Measurement of the reduction in interfacial tension between refined cottonseed oil and water produced by various percentages of monoesters of several distilled monoglyceride products.

In Figure 8 water absorption values are plotted for varying percentages of glyceryl monoesters of cottonseed oil in the oil phase. In this graph the ordinate values are 10 times and the abscissa units 1/10 of those shown for the stearic acid monoglycerides. Thus comparable amounts of unsaturated monoglycerides are approximately 100 times more effective in forming this type of emulsion than the saturated monoglycerides. In this plot a distilled product of cottonseed oil containing 93% monoester is compared to a laboratory prepared reaction mixture of cottonseed oil containing 42% monoester. It is apparent that in this case the rest of the reaction mixture adds to the emulsifying properties of the monoester.

Summary

Monoglyceride concentrates of high purity can be readily prepared by molecular distillation. Their properties are, in general, about what would be expected from the high content of monoglycerides and absence of catalyst.

The interfacial tension lowering produced by monoglycerides is essentially proportional to the monoester content of the monoglyceride product. In a water absorption test the unsaturated fatty acid monoglycerides are considerably more active than the monoesters of saturated fatty acids.

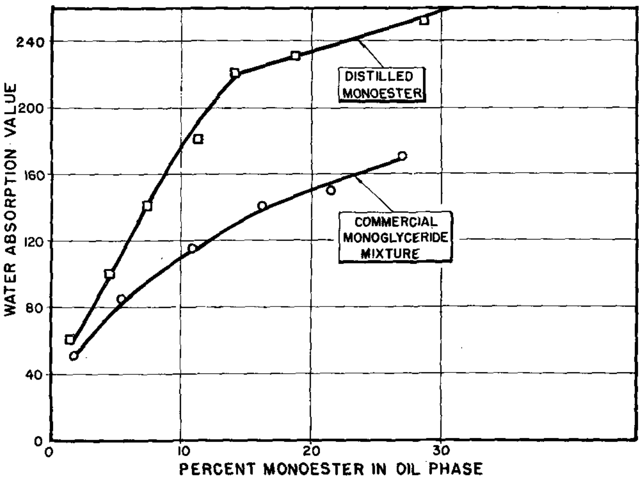

Fig. 7. The effect of monoesters from triple-pressed stearic acid monoglyceride products on the stabilization of a w/o emulsion. The curves indicate the volume of water in ml. held in a stable emulsion by 100 grams of petrolatum containing monoglycerides.

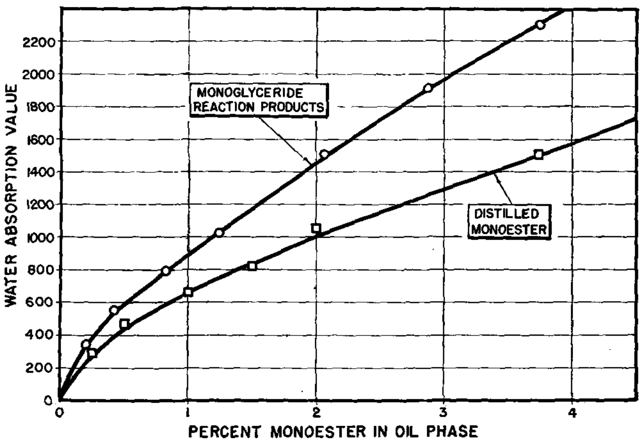

Fig. 8. The effect of monoesters from cottonseed oil monoglyceride products on the stabilization of a w/o emulsion. The curves indicate the volume of water in ml. held in a stable emulsion by 100 grams of petrolatum containing monoglycerides.

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