The Preparation and Properties of Highly Purified Methyl Oleate‡

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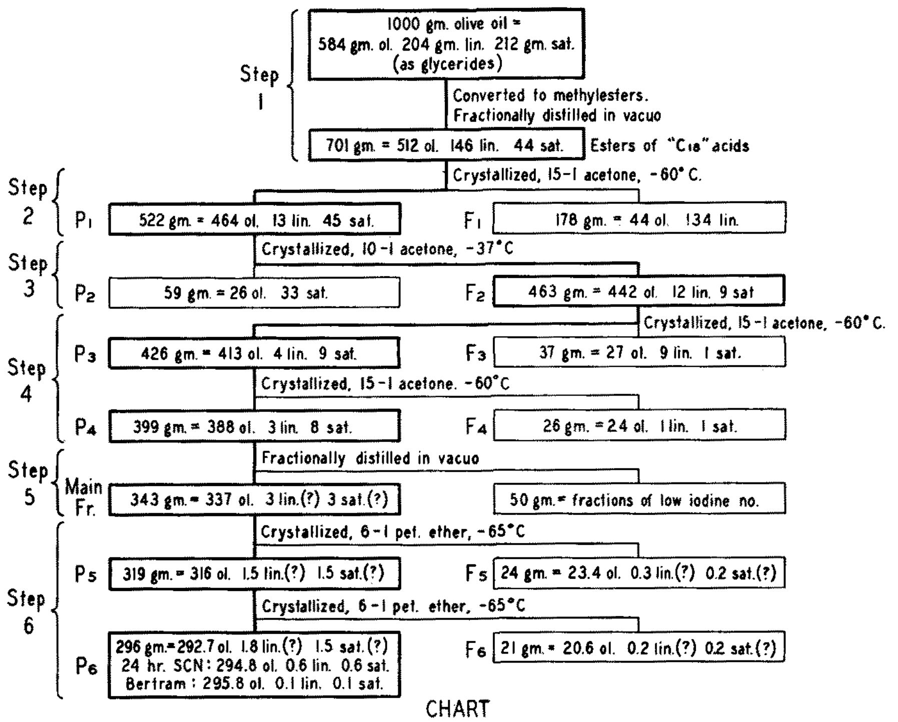

CHART
WEIGHT SUMMARY OF STEPS IN PURIFICATION OF METHYL OLEATE

Fig. 1.

OF THE common unsaturated acids occurring in edible fats and oils, oleic acid is one of the most difficult to obtain in pure form. It does not afford a crystalline bromine addition compound which is readily purified and from which the pure acid can be regenerated. Methods of separation from other acids do not appear to be complete or convenient. Since appreciable quantities of oleic acid of a very high degree of purity were desired for the synthesis of certain glycerides, a review was made of the various methods for its preparation. A number were tried and the recent method of Brown and Shinowara (1) for its preparation by low temperature crystallization of the acids of olive oil seemed to offer the best possibilities. However, when this method was tried, it was found that the product contained appreciable amounts of palmitic acid. Fractional distillation gave considerable quantities of lower boiling fractions of low iodine number which deposited palmitic acid on cooling. Since these results indicated that careful fractionation would be necessary to remove palmitic acid, and since the methyl esters are more suited to fractional distillation than are the acids, it was decided to investigate the possibilities of working with the methyl esters instead of the acids.

Preliminary experiments did show that methyl oleate could be crystallized from 10 to 20 volumes of acetone at -60° C. with good recovery, and that methyl linoleate remained in solution in the filtrate. It was also found that the saturated esters could be removed by fractional distillation in vacuo. The final method consisted of a number of low temperature crystallizations and two fractional distillations in vacuo.

The analytical methods used in following each step in the purification and in testing the final product have been evaluated in another paper (2). It is felt that such analyses on the products of the various steps should afford good criteria of the efficiency of the method and help in evaluating the purity of the final product.

Apparatus and General Methods

Fractional distillations were carried out with an electrically heated column 600 mm. in length and 35 mm. diameter, packed with small glass helices and equipped with a total reflux, partial take-off distilling head. For the low temperature crystallizations, solid CO_2 was used as the cooling agent. In the acetone crystallizations, the mixture was cooled by direct addition of solid CO_2, while in the petroleum ether crystallizations an external CO_2 — alcohol bath was used, and the mixture stirred with a mechanical stirrer. Filtrations were carried out by suction, in a room at -18°C. The Büchner funnels were always chilled by pouring through them a portion of solvent cooled to the temperature of crystallization. Filtrations were quite rapid.

Procedure: The steps involved in the purification are as follows:

1. Fractional distillation of the methyl esters of the mixed acids of olive oil, to remove palmitic and lower esters.
2. Removal of most of the linoleic ester (in the filtrate) by crystallization from acetone (15 cc. per gm. ester) at -60° C.
3. Precipitation of the bulk of the saturated esters from acetone (10 cc./gm.) at -37° C. and removal by filtration.
4. Further elimination of methyl linoleate by two crystallizations from acetone (15 cc./gm.) at -60° C.
5. Fractional distillation in vacuo to remove small amounts of remaining methyl palmitate.
6. Two crystallizations (at -65° C.) from redistilled petroleum ether (6 cc./gm.) (b.p. 30° -45° C.) to remove last traces of linoleate.

The results of the analyses of the fractions obtained by this procedure are shown in the table below. The "P's" and "F's" refer

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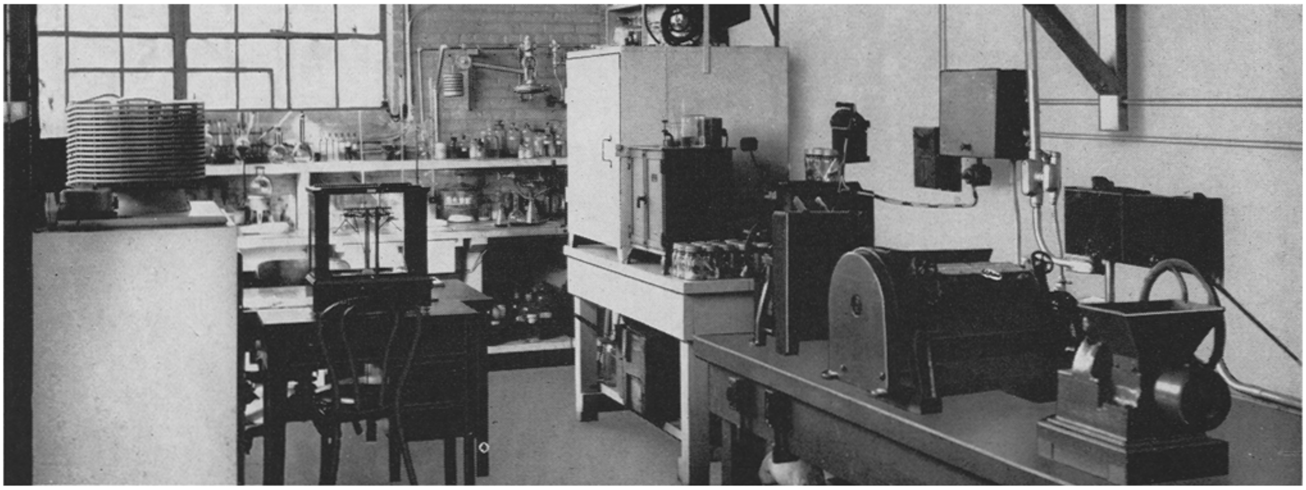
A MODERN LABORATORY SOAP PLANT



The Hooker Electrochemical Company at Niagara Falls have developed a rather unique laboratory-scale soap plant with complete manufacturing and analytical facilities. In the above view a battery of three thermostatically controlled soap kettles are not visible, while other equipment partially shown above includes a special experimental crutcher, and other necessary equipment such as mill, plodder and press, thus permitting any variety of cold process, chip, or milled toilet soap to be manufactured.

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to precipitate and filtrate, respectively, of the crystallizations. The underscored data are for the fractions in which the bulk of the methyl oleate is present.

It will be noted that the last two crystallizations did not change the iodine number, and that this value is identical on the last precipitate and filtrate. From the data in the table, the chart shown below has been constructed to show the weight of each constituent of the various fractions. The weights of the fractions shown have been corrected for samples removed for analysis. These weighed samples were taken from each of the fractions, distilled in vacuo, and analyzed. Fig. 1.

The olive oil used was purchased as U.S.P. olive oil and had unusually high content of linoleic and saturated acids. This fact might indicate that fewer steps would be necessary on an oil of higher oleic acid content.

It will be seen from this chart that the preliminary distillation removed much of the saturated esters which were largely palmitic. Step 2 removed over 90 percent of the linoleic ester present, and Step 3 eliminated some three-fourths of the remaining saturated esters. Step 4 practically completed the removal of the remaining linoleate. Distillation of a small portion of the product at this point indicated that most of the remaining saturated esters was palmitic. Therefore, the main portion, P-4, was fractionally distilled (Step 5) and small fractions of distillate (1 percent to 2 percent of the total) were collected until the iodine value showed no increase on two successive fractions and was within 0.3 unit of theory for methyl oleate. The main fraction was then collected. The weights given in the chart for minor components are only approximate from this point on, as the analytical methods are approaching their limit of accuracy. The last step, No. 6, indicates that purification had been carried as far as practical by the methods here described.

From the data in Table 2 and especially the more complete analyses of P_5, F_5, P_6 and F_6 it seems certain that the final product, P_6, had a purity of 99 percent or better. It should be realized that while the three-hour thiocyanogen number is to be recommended as most suitable for analysis of mixtures containing relatively large amounts of linoleic ester (2), the accuracy when applied to nearly pure methyl oleate is not sufficient to be a very precise criterion of purity. As shown in the table, the twenty-four-hour thiocyanogen number indicates 99.6 percent oleic with 0.2

TABLE OF RESULTS OF ANALYSES OF FRACTIONS FROM PREPARATION OF METHYL OLEATE

STEP	MATERIAL	IODINE № WIJS ½ HR.	SCN. № 3 HR.	% OLEIC	% LINOLEIC	% SAT.	% SAT. BERTRAM
1	OIL	85.3	67.8	58.4	20.4	21.2	20.7
	C_{18} ESTERS	98.5	80.5	73.0	20.9	6.1	5.9
2	P-1	80.5	78.3	88.8	2.6	8.6	
	F-1	150.9	86.1	24.8	75.2	0.0	
3	P-2	37.1	—	43.5	—	56.5	
	F-2	86.2	84.0	95.4	2.6	2.0	
4	P-3	84.9	84.0	97.0	1.0	2.0	
	F-3	104.7	83.6	73.0	24.5	2.5	
	P-4	84.5	83.9	97.2	0.7	2.1	
	F-4	86.1	82.5	92.1	4.2	3.7	
5	MAIN FRACTION	85.8	85.0	98.3	0.9	0.8	
6	P-5	85.7	85.3	99.1	0.5	0.4	0.08
	F-5	86.0	84.8	97.6	1.4	1.0	0.06
	P-6	85.7 *	85.2	98.9	0.6	0.5	
	"	85.7	85.5 ‡	99.6	0.2	0.2	
	"	85.7	—	99.9	0.04	0.04	0.04
	F-6	85.7	84.8	98.0	1.0	1.0	0.08
	THEORY, METHYL OLEATE	85.7	85.7				

* HANUS IODINE № ½ HR. = 85.7

‡ 24 HR. SCN. №

Table 2.

percent each of linoleic and saturated esters. It is believed that the Bertram value for saturated esters is essentially correct, and that the final product does not contain more than 0.1 percent of saturated or linoleic ester.

The product thus obtained was found to have the following physical properties:

	20°C	25°C.
Refractive index, n^{t}_{d}	1.4522	1.4502
Density $\frac{t}{4°}$ (corr. to vacuo)	0.8739	0.8704
Melting Point (capillary)	-19.9° to -19.6° C.	

Keffler and McLean (3) give 0.8738 and 0.8702 for densities at 20° and 25° respectively.

Oleic acid prepared from the ester in the usual manner and distilled in vacuo had the following constants:

Iodine no. (Wijs ½ hr.)	90.0
Thiocyanogen no. (3 hr.)	89.6
Refractive index n^{t}_{d}	1.4599 (20°), 1.4581 (25°)
Melting Point (capillary)	+13.0° to +13.2° C. and +16.0° to +16.3° C.

The refractive index shown is higher than that given by Brown (1) (n^{20}_{d}=1.4585) and lower than the value reported by Skellon (4) (n^{20}_{d}=1.4610). Others have reported similar values. The dimorphism observed has been previously reported, by Raymond (5) (m.p.'s 13° and 16° C.), Robinson (6) (m.p.'s 13° and "just above" 16° C.) and others.

Summary

1. Methyl oleate of high purity has been prepared by fractional distillation and low temperature crystallization of the methyl esters of the acids of olive oil.

2. The steps involved in the purification have been followed by analysis of each fraction.

3. Some physical and chemical properties of the purified methyl oleate and of oleic acid obtained from it have been reported.

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Solidification Point Curves of Binary Acid Mixtures

I. Capric, Lauric, Myristic, Palmitic

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THE older conventional methods for separating the saturated acids of a fatty oil are essentially applications of fractional crystallization or precipitation techniques. A newer, more satisfactory, method of analysis rests upon the fractional distillation of the fatty acids as their lower alkyl esters. In both types of procedures the objective is reached when several fractions, each of different mean molecular weight, have been obtained. Given ample quantities of material, it is true that by laborious and painstaking effort these separations can occasionally be made to yield fractions corresponding, in molecular weight, to a pure, or nearly pure, fatty acid; but ordinary separations stop at a point at which each fraction contains a major proportion of a fatty acid and a lesser one of the next higher or lower homolog. For the purpose of arriving, then, at the composition of each fraction the mean molecular weight is determined from the saponification value and calculation is made of the composition represented by that value. Such a calculation is, of course, valid mathematically, yet it is nevertheless empirical in that it assumes the presence of the pair of acids selected, since, for example, a mixture of mean molecular weight between that of lauric and myristic acids does not necessarily indicate this pair, for it might just as well represent a mixture of lauric and palmitic acids, but in somewhat different proportion.

There exists an obvious need, therefore, for some means of corroborating calculations of this type, when they are pertinent to natural mixtures, insofar as they effect conclusions based upon the assumed presence of any given pair of acids in them. In this communication we suggest that the use of solidification point curves of binary fatty acid mixtures will meet that need.

Solidification point curves have long been a valuable analytical tool in the inorganic field; especially in that of metals and alloys has thermal analysis been very widely used and extensively developed. Although these principles have been applied by others to some extent to the long-chain fatty acids, yet there exist sufficient gaps in the homologous series of these compounds to warrant further study in this field. Herein recorded are the curves representing mixtures of capric-lauric, lauric-myristic, and myristic-palmitic acids.

The fatty acids used in this study were recovered from commercial products* of *ca* 90 per cent purity. The method of purification used varied somewhat with the acid but the general procedure followed was that of esterification, bromination, and fractional distillation. Methyl esters were prepared by the method

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