TABLE II

Summary of Performance Data [a]

Sample	Reagent	Per cent reagent	Wetting time [b]	Foaming power		Detergency [c]			
						DW [f]		HW [g]	
				DW [e]	HW [d]	0.05	0.1	0.05	0.1
C-1-1	Sulfamic	105	17	155	170	20	36	36	35
C-1-1	SO_3	100	20	160	190	11	32	29	36
C-1-1	SO_3	105	18	160	210	10	33	34	36
C-1-1	SO_3	110	20	160	220	9	32	33	36
C-1-1	SO_3	195	171	125	200	4	8	5	14
D-2	Sulfamic	105	26	120	210	2	17	15	31
D-2	SO_3	110	28	185	210	5	17	16	27
E-1	Sulfamic	110	26	145	130	32	20	34	38
E-1	SO_3	110	32	140	140	38	36	38	40

[a] All samples showed excellent resistance to 15° hard water at 0.2%.
[b] Draves (Synthron Tape Method) in seconds at 25°C., 0.1% solution.
[c] Ross-Miles in distilled water at 0.05%.
[d] Ross-Miles in 15° hard water at 0.1%.
[e] Expressed as percentage of brightness increase of wool in Launder-Ometer.
[f] In distilled water at percentages given.
[g] In 20° hard water at percentages given.

tion with 195% sulfur trioxide strongly impairs all properties except hard-water foaming power. With octylphenol-5 ethylene oxide (D-2) the two reagents give sulfates of very similar performance except that the sulfur trioxide-based material has considerably better distilled water-foaming power. In general, this sulfate is a less effective detergent and wetting agent than that derived from nonylphenol-4 ethylene oxide regardless of reagent used. In the case of sample E-1 (dodecylphenol-6 ethylene oxide) the two reagents show similar performance, with possibly slightly better detergency and slightly greater wetting-time for sulfur trioxide.

Comparison of the performance data obtained in the present study with that reported recently by the present authors for the sulfated ethenoxylated long-chain alcohols (6) shows the alkylphenol-based products to advantage. Two of the alcohol-derived sulfates (B and D) gave nearly the same foaming-power as those made from the alkylphenol, but wetting time and detergency were considerably inferior. The third alcohol-based sulfate (E) showed substantially better detergency than the other two (but still lower than the alkylphenol-derived material); however it had comparatively poor foaming-power and wetting time.

Sulfating Agents Compared

The major conclusions from this study may be summarized as follows. Per unit weight of sulfur trioxide introduced, sulfur trioxide costs approximately one-seventh as much as sulfamic acid and involves about one-sixth of the reaction time. Sulfur trioxide gives lighter product color and allows formation of any desired-product salt while sulfamic acid gives the ammonium salt, which can be converted to other salts (*e.g.*, sodium) only with difficulty. On the other hand, sulfur dioxide gives appreciable foaming during sulfation while sulfamic acid gives none. Sulfur trioxide must be vaporized while sulfamic acid is added directly. Ring sulfonation with sulfur trioxide is appreciable, but none occurs with sulfamic acid. Product performance with the two reagents appears comparable however.

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Pure Oleic Acid from Olive Oil

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IN THE PAST 23 years a number of new techniques have been developed for the preparation of oleic acid from olive oil. Both olive oil acids and methyl esters have been submitted to purification. The use of low-temperature (−60°C.) solvent crystallization for this purpose, combined with fractional distillation, is described in "Biochemical Preparations" (1), where earlier literature references are given.

The discovery of urea inclusion compounds in 1949 —a general review, as applied to fatty acids, is given by Schlenk (2)—provided yet another tool for fatty acid (or ester) fractionation. It was used by Schlenk

and Holman (3), who prepared methyl oleate (97–98% pure) in 40% yield from olive oil methyl esters; Swern and Parker (4) obtained a 60% yield of oleic acid (97.7% pure), containing 0.1% linoleic acid and 2.2% saturated acids.

More recently Smull (5) and Meade (6) reported a new development in the separation of fatty acid mixtures. The differences in the solubilities of the acid soaps of saturated, mono-unsaturated, and polyunsaturated fatty acids are sufficient to allow separation by crystallization. Smull utilized this fact to separate oleic acid from the other components, primarily linoleic acid, of tall oil fatty acids. Kairys, Meade, Munns, and Walder (7) were able to separate saturated from unsaturated fatty acids *via* the acid soaps in an aqueous system. The term "acid soap" refers to the compound containing one molecule of e.g. sodium oleate for each molecule of oleic acid (8).

Keppler *et al.* (9) have just published a note on the preparation of pure oleic acid by urea-adduct separation and fractional distillation, followed by treatment with maleic anhydride and iodine to remove the remaining small amounts of linoleic acid. They obtained a 23% yield of oleic acid containing a few tenths of 1% of saturated acid; however 5% of the oleic acid was converted to the *trans* isomer by the maleic anhydride-iodine treatment.

By a combination of urea-adduct precipitation and acid soap crystallization we were able to obtain oleic acid of 99–100% purity from olive oil. Two urea-adduct fractionations of the olive oil fatty acids at room temperature served to reduce the total saturated acid content to about 1%. Stearic and arachidic acids were completely removed; only a small amount of palmitic acid remained. The removal of stearic acid is especially noteworthy since it could not be achieved by distillation. Three acid soap crystallizations of the remaining fatty acids eliminated the polyunsaturated acids, plus traces of palmitoleic and palmitic acids, giving an excellent product (99–100% pure, no *trans* isomer) in 36–43% yield. The method was scaled up to handle 5 kg. of olive oil. Olive oil methyl esters may be used for the urea fractionations, but it is preferable to start with the fatty acid mixture since the free acids are required for the acid soap crystallizations.

Experimental

Five kg. of California olive oil were saponified under nitrogen, modifying slightly the procedure described in "Biochemical Preparations" (1). Extracting the fatty acid mixture with hexane, and drying the hexane extract over anhydrous sodium sulphate, greatly facilitated the working-up of the product.

Urea-Adduct Separation. The warm (50°C.) fatty acid mixture (4.95 kg.) was added, with mechanical stirring, to a warm solution of 5 kg. of urea in 15 liters of methanol. A heavy, white precipitate formed, and the mixture was allowed to cool to room temperature. After standing over-night, the crystals were filtered off on a Buchner funnel and washed well with a saturated solution of urea in methanol (16 g. per 100 ml.). Washing with this solution decreases the possibility of decomposing the adducts and makes for better separations and easier handling. Most of the methanol was removed from the filtrate *in vacuo;* the residue was taken up in water, acidified with dilute hydrochloric acid, and extracted with hexane. After the hexane layer had been washed well with water, it was dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* to give 3.81 kg. (77%) of fatty acids. A second treatment with urea (2.86 kg. in 11.5 liters of methanol) resulted in 2.82 kg. (74%) of fatty acids with the following composition:[1]

	%
palmitic	1.5
palmitoleic	0.86
stearic	trace
oleic	87.1
linoleic	10.6
linolenic	trace

Acid Soap Crystallizations. Sodium hydroxide solution was prepared to contain 0.0656 g. of sodium hydroxide per ml. of 80% methanol. This solution was diluted five times for use in titrations. By titrating 1 g. of the fatty acids to a phenolphthalein end-point, the volume of sodium hydroxide solution required to form the normal soaps was determined. Half of this quantity was then used to obtain the acid soaps.

To a warm solution of 2.78 kg. of the above fatty acids in 2.78 liters of methanol were added 2.89 liters (amount calculated from titration) of the methanolic sodium hydroxide solution. This gave a crystallization mixture of 2.0 ml. of 90% methanol per g. of fatty acids. The acid soaps were allowed to crystallize overnight at 3°C. They were filtered off in a cold room at 3–5°C. and washed well with cold 80% methanol. (A slurry was made with the wet cake and wash liquid.) By drying a small portion, the wet cake was calculated to contain 1.56 liters of 80% methanol and the equivalent of 2.00 kg. of fatty acids. The addition of 1.44 liters of methanol gave a solvent mixture of approximately 90% methanol (1.5 ml./g. of fatty acids). The acid soaps were brought into solution by warming, allowed to crystallize as before, filtered, and washed. As pointed out below, the volume of 90% methanol for this and the third crystallization could be increased advantageously to 2.5 ml. per g. of fatty acids.

This recrystallization procedure was carried out once more. The wet acid soap was then treated with an excess of 5% hydrochloric acid. The oily upper layer which formed was extracted with hexane; the hexane layer was washed with water, dried over sodium sulphate, and evaporated *in vacuo* to give 1.65 kg. of pale yellow product. The yield of oleic acid was 43.4%, based on the oleic content of the olive oil acids. $n^{26/D} = 1.4573$; I.V. 89.4 (theor. 89.9).

Runs varying in size from 100 g. to 5 kg. of starting material were carried out. In the 5-kg. run the final product was pale yellow in color in spite of intensive washing during the acid soap filtrations. Gas-liquid chromatography indicated a purity of 99+% but also showed traces of a contaminant, which was not fatty acid. In other runs (up to 1 kg. in size), after each crystallization, the acid soaps were converted back to the fatty acids, which were then dissolved in 1.5 ml. of methanol per g. Enough 80% methanolic sodium hydroxide solution (about 1 ml./g.) was added to form acid soaps. This made a total volume of about 2.5 ml./g. The contaminant mentioned was not present, and the product was almost colorless. Therefore the increase in volume of solvent for the direct crystallization of the acid soaps is recommended.

A portion of the product from the 5-kg. run was distilled at 195–197°C./2 mm., giving a clear, colorless liquid in 89% yield. The gas chromatogram

[1] Compositions were determined by gas-liquid chromatography on an Aerograph A90, using a succinic acid-diethylene glycol polyester column (10), with helium as the carrier gas.

showed no impurities; infrared analysis proved that no *trans* isomer was present. I.V. 90.5 (theor. 89.9); acid value 198.7 (theor. 198.6); $n^{26/D} = 1.4585$ [Lit. $n^{20/D} = 1.4585$, 1.4599 (1)].

Preparation of Derivatives. Methyl oleate was prepared from our oleic acid (99+%, undistilled), and distilled at 168–170°C./2 mm. to give a clear, colorless product. The gas chromatogram showed no impurities. I.V. 85.8 (theor. 85.6); $n^{26/D} = 1.4510$, Lit. $n^{20/D} = 1.4522$ (1).

Oleoyl chloride was prepared by refluxing undistilled oleic acid, in dry benzene, with oxalyl chloride (11). The crude material was distilled at 169–170°C./4 mm. to give a clear, colorless product in 87% yield. Infrared analysis revealed no trace of oleic acid or other contaminants.

Reduction with lithium aluminum hydride of the methyl oleate made from oleic acid (both undistilled) gave oleyl alcohol in quantitative yield (12). The undistilled product had a saponification value of zero and an I.V. of 93.2 (theor. 94.5). When analyzed in the gas chromatograph as the acetate, no impurities were detected.

Summary

Oleic acid of 99–100% purity has been prepared in 36–43% yield from olive oil. The combination of two urea-adduct separations (at room temperature) and three acid soap crystallizations (at 3°C.) gives an oleic acid of high quality without recourse to fractional distillation or low-temperature solvent crystallization.

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The Enzymatic Hydrolysis and Tissue Oxidation of Fatty Acid Esters of Sucrose[1]

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FATTY ACID ESTERS of sucrose have been employed (1) as emulsifiers for the oral administration of fat to dogs and humans. It was subsequently found that the equivalent of as much as 100 g. of fat as the sucrose fatty acid ester in a synthetic diet could be orally administered without the expected elevation of plasma turbidity or increase in the amount of fat excreted in feces (2). In an extension of these studies, humans were maintained for short periods on this material as the sole source of dietary lipid. In an attempt to determine whether some unusual mode of absorption of sucrose fatty acid might be involved, various modes of enzymic attack were studied. Quastel (3) reported that sucrose monostearate was hydrolyzed to glucose and fructose by surviving intestine at one-fourth the rate of sucrose hydrolysis; and York, Finchler, Osipow, and Snell (4) reported the hydrolysis of sucrose monolaurate by fructo-invertase. However Bourne (5) was unable to demonstrate hydrolysis of sucrose monostearate by α-amylase or by gluco- or fructo-invertase. Sucrose fatty acid esters were found by Isaac and Jenkins (6) to be capable of supporting oxidation by sewage.

The present communication describes the effect of lipase, invertase, and liver and pancreatic extracts on various commercial preparations of sucrose fatty acid esters and the oxidation of these preparations by homogenates of liver and intestinal mucosa.

Experimental

Material. Sucrose fatty acid esters used were "Sequol 260"[2] (22% palmitic acid, 3.4% stearic acid, 22% oleic acid, 47% linoleic acid); sucrose monopalmitate[3] (89% palmitic acid, 4.3% stearic acid); sucrose monostearate A[4] (42% palmitic acid, 44% stearic acid, 5.4% oleic acid); sucrose monostearate B[5] (39% palmitic acid, 53% stearic acid, 3% oleic acid); sucrose di-,[6] tri-,[7] and tetralinoleate[8]; and the transesterification product[9] of sucrose and safflower oil.

Procedure. A 1% solution of each sucrose fatty acid ester was made up with 20 ml. 95% ethanol and 80 ml. glycerol. Each incubation vessel contained 50 μmoles sucrose ester, 70 μmoles Tris(hydroxymethyl)-aminomethane buffered at pH 8.1, 50 μmoles sodium taurocholate or sodium glycocholate, 100 μg. enzyme

[1] This work was carried out under U.S.P.H.S. Grant No. A-1808 and Sugar Research Foundation Grant No. 109.

[2] Supplied by the Charles Pfizer Company and prepared as the transesterification product of sucrose and cottonseed oil.
[3] Sucrodet D-600, Berkeley Chemical Company, Lot No. S-187.
[4] Ottawa Chemical Company, Batch No. 7255 (8/10/55).
[5] Foster D. Snell, Batch No. 596.
[6] Colonial Sugars Company (7-L-184/5-22-59).
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