Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols.[1] II. Oleic Acid and Methyl Oleate From Olive Oil[2]

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THE use of urea complexes in the preparation of oleic acid of 80-95% purity in good yield from various commercially available inedible animal fat sources was recently reported by us (4). In this paper we are describing the use of urea complexes in the isolation of oleic acid and methyl oleate from olive oil, employing the "single dose of urea" technique first described in our previous paper (4).

Schlenk and Holman (2) were apparently the first workers to employ urea complexes in the preparation of purified methyl oleate (purity, 97-98%) from olive oil. These investigators employed a stepwise addition of urea which was designed to remove first two successive 10% portions of the olive oil methyl esters as urea complexes (to eliminate saturated methyl esters), followed by a precipitation of the bulk of the remaining esters (mostly methyl oleate) as urea complexes, leaving most of the methyl linoleate in the final filtrate (non-complex fraction). Fractional distillation of the methyl oleate was again followed by urea treatment. For reasons given in our previous paper (4), with olive oil acids or methyl esters, we prefer to use a single dose of urea to precipitate both saturated and monounsaturated materials as urea complexes in one step, leaving the polyunsaturated materials in the filtrate, and, if necessary, separate saturates from the oleic acid or methyl oleate by solvent crystallization and/or fractional distillation.

Experimental

Materials Used. Urea and methanol were the purest available reagent grades. California olive oil (iodine number, 78.0) was employed and had the following fatty acid composition (1): oleic acid, 80.2%; linoleic acid, 3.7%; linolenic acid, 1.0%; saturated acids, 15.1%. The fatty acids (iodine number, 81.3) were prepared in quantitative yield by the rapid saponification technique previously reported (3).

Purification of Oleic Acid (Solution Method). One thousand grams of olive oil fatty acids were dissolved in a boiling solution of 3,600 g. of urea in 9,000 ml. of methanol. Crystals of urea complexes formed as soon as the container was removed from the steam bath. The mixture was cooled to 0° overnight and filtered, yielding 3,870 g. of urea complexes. These were stirred with a large volume of hot water to dissolve the urea, yielding 840 g. of almost colorless oil as an upper layer (iodine number, 77; composition: oleic acid, 83.9%; linoleic acid, 0.9%; saturated acids, 15.2%). The yield of oleic acid recovered to this point was 88%. Fractional distillation through a 10-plate column yielded 432 g. of a lower, semi-solid fraction, b.p. 192-205°/4 (iodine number, 64.9), and 380 g. of colorless, odorless oleic acid, b.p. 205-206°/3.9 (iodine number, 82.8; composition: oleic acid, 90.4%; linoleic acid, 0.9%; saturated acids, 8.7%). The overall yield of oleic acid recovered was 43%.

To obtain a higher purity and polyunsaturate-free oleic acid, as well as a better overall yield, the acids isolated from the complex were fractionally crystallized from acetone (12 ml./g.) prior to distillation. From 840 g. of these (iodine number, 77), 140 g. of saturated acids (iodine number, 16) were obtained as a precipitate at −20°; 620 g. of an oleic acid fraction (iodine number, 85; composition: oleic acid, 94.4%; linoleic acid, 0.1%; saturated acids, 5.5%) were obtained as a precipitate at −50°. The yield of oleic acid recovered to this point was 72%. Fractional distillation of the precipitate obtained at −50° yielded 500 g. of colorless, odorless liquid (iodine number, 88.0; composition: oleic acid, 97.7%; linoleic acid, 0.1%; saturated acids, 2.2%). The final yield of oleic acid was 60%.

Purification of Oleic Acid (Slurry Method). In the slurry method the volume of methanol is reduced to one-half that used in the Solution Method and the time is shorter. In a stainless steel kettle a slurry was prepared consisting of 3,600 g. of urea and 4,500 ml. of methanol. To the well-stirred slurry 1,000 g. of olive oil acids were added at such a rate that the temperature did not exceed 35°. The slurry was stirred until the internal temperature had fallen approximately to room temperature (this required about 8 hours), and the mixture was filtered. The urea complexes weighed 3,680 g. from which 900 g. of almost colorless oil was obtained (iodine number, 78; composition: oleic acid, 85%; linoleic acid, 1%; saturated acids, 14%). Subsequent processing and results were approximately the same as just described under Solution Method except that yields of oleic acid recovered at each step were about 5% higher.

Purification of Methyl Oleate (Solution Method). Three grams of freshly cut metallic sodium was dissolved in 5,000 ml. of anhydrous methanol. One thousand grams of olive oil were added and the solution was refluxed for 30 minutes. An additional 5,000 ml. of methanol and 3,600 g. of urea were then added, and the mixture was boiled until the urea dissolved. The reaction mixture was cooled to 20° and filtered, yielding 3,400 g. of urea complexes. These were stirred with hot water to dissolve the urea yielding 790 g. of a methyl oleate fraction (iodine number, 71.4; composition: methyl oleate, 81.5%; methyl linoleate, 0.9%; saturates, 17.6%), as an almost colorless upper layer. The methyl oleate recovered to this point was 80%. Fractional distillation yielded 170 g. of lower fraction, b.p. 164-179°/4 (iodine number, 50.2), and 550 g. of colorless, odorless methyl oleate fraction, b.p. 180-1°/4 (iodine number, 78.0; composition: methyl oleate, 89%; methyl linoleate, 1%; saturates, 10%). The overall yield of methyl oleate recovered was 61%.

[1] The first paper in this series is reference 4.

[2] Presented at the Fall meeting of the American Oil Chemists' Society, Cincinnati, Ohio, Oct. 20-22, 1952.

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Fractional crystallization from acetone (10 ml./g.) of 790 g. of methyl oleate (iodine number, 71.4), recovered from the urea complexes, yielded 140 g. of saturated methyl esters (iodine number, 15) at −35°; 580 g. of methyl oleate (iodine number, 83.5; composition: methyl oleate, 97.2%; methyl linoleate, 0.2%; saturates, 2.6%) was obtained as a precipitate at −60°. The yield of methyl oleate recovered to this point was 70%. Fractional distillation of the methyl oleate fraction yielded 540 g. of methyl oleate, b.p. 184°/4.2 (iodine number, 84.9; composition: methyl oleate, 98.9%; methyl linoleate, 0.2%; saturates, 0.9%). The final yield of methyl oleate recovered was 66%.

Purification of Methyl Oleate (Slurry Method). The methanolysis of olive oil was carried out as described earlier, but at its completion no additional methanol was added. The reaction mixture was cooled to room temperature and 3,600 g. of urea were then added. The slurry was stirred until the reaction temperature had again reached room temperature (about 8 hours were required). The mixture was filtered, yielding 3,870 g. of complexes from which 812 g. of methyl oleate (iodine number, 73.4; composition: methyl oleate, 83.8%; methyl linoleate, 1.0%; saturates, 15.2%) was obtained. Subsequent processing and results were approximately the same as just described under Solution Method except that yields of methyl oleate recovered at each step were about 5% higher.

Discussion

Oleic acid and methyl oleate of high purity (97-99%) and substantially free (0.2% or less) of polyunsaturated contaminants can be obtained in good yield (60-70%) from the fatty acids or methyl esters of olive oil by procedures which require only one precipitation of urea complexes, one low-temperature crystallization, and one fractional distillation. In the purification of methyl oleate it is not necessary to isolate the mixed methyl esters of olive oil because the urea complex precipitation technique can be applied directly to the methanolysis reaction mixture.

"Recrystallization" of urea complexes from methanol does not separate the polyunsaturated contaminants completely and merely reduces the overall yield of oleic acid recovered. If a polyunsaturate-free oleic acid or methyl oleate is not required, the low temperature crystallizations can be eliminated entirely. If low temperature facilities are not available or are inconvenient to set up, the urea complex technique permits the preparation of oleic acid or methyl oleate sufficiently low in polyunsaturated contaminants for many chemical investigations.

To obtain the best yields of fractionally-distilled oleic acid it is necessary, after decomposition of the urea complexes, to precipitate the saturated fatty acids, particularly palmitic acid, which are still present. For each gram of palmitic acid which must be separated by distillation, as much as two grams of oleic acid will be distilled along with it even when efficient fractionating columns are used. This undesirable phenomenon, which does not occur with methyl esters, is probably caused by azeotrope formation. Thus fractional distillation of the fatty acids obtained from the urea complexes (palmitic acid present) gives an overall yield of recovered oleic acid of 43-48%, fractional distillation after separation of saturated acids by solvent crystallization (palmitic acid substantially absent) gives 60-65% yields, and distillation of methyl esters (methyl palmitate present or absent) also gives 60-65% yields.

Summary

Oleic acid and methyl oleate of high purity (97-99%) and substantially free (0.2% or less) of polyunsaturated contaminants have been isolated in 60-70% yield from the fatty acids or methyl esters of olive oil by procedures which require only one precipitation of urea complexes (single dose of urea technique) one low-temperature crystallization, and one fractional distillation. The best yields of the highest purity acids are obtained when saturates are removed by fractional crystallization prior to a final distillation. The urea complex separation technique can be applied directly to olive oil methanolysis reaction mixtures without prior isolation of the mixed methyl esters.

Oleic acid or methyl oleate obtained by decomposition of urea complexes contains approximately 1% of polyunsaturated contaminants. After fractional distillation or crystallization to separate saturated acids the oleic content is about 90-97%. Such products are satisfactory for many uses and in their preparation low-temperature (−50° or lower) crystallizations are not required.

Solution and slurry techniques have been studied for the preparation of urea complexes from olive oil acids or esters. The former technique is preferred when a maximum of about 1,000 grams of acids or esters are to be processed. The latter is preferred for larger size experiments mainly because the volume of methanol employed is cut in half, the time is shorter, and also because yields are about 5% higher.

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2. Schlenk, H., and Holman, R. T., J. Am. Chem. Soc., *72*, 5001-5004 (1950).
3. Swern, Daniel, Knight, H. B., Scanlan, J. T., and Ault, W. C., Oil & Soap, *22*, 302-304 (1945).
4. Swern, Daniel, and Parker, W. E., J. Am. Oil Chem. Soc. (in press).

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CORRECTION

Corrections for the paper entitled "The Aliphatic Alcohols of Wool Wax. V. Studies in Waxes," by K. E. Murray and R. Schoenfeld, published in the October 1952 issue of the Journal (*29*, 416-420) are as follows:

Reference 3 should read:
Darmstädter, L., and Lifschütz, J., Ber. *29*, 2890 (1896).

Reference 10 should read:
Knol, H. W., Dutch Pat. 65,260 (1950). U. S. Pat. 2,536,753 (1951). Br. Pat. 626,299 (1950).