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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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).