Letter to the Editor

September 20, 1956

IT HAS BEEN SHOWN recently (1) that alkali catalyzed methanolysis makes possible the preparation of methyl esters from triglycerides in an almost quantitative yield. The method is applicable only to fats with low acid values since free fatty acids not only escape conversion into esters but, by reacting with the catalyst with the formation of water, affect the methanolysis of glycerides. However even fats which require saponification with alkalis can be converted into methyl esters without first isolating fatty acids. Youngs and Craig (2) suggested direct conversion of soaps into methyl esters by double exchange with dimethyl sulphate, but in most cases the refluxing of methanolic soap solution with a calculated quantity of sulphuric acid will also give satisfactory results.

The conventional procedure of separating free fatty acids before the esterification has been apparently based on the assumption that water formed during the acidification of soaps might interfere with ester formation. If however the alkali hydroxide is used in 50% excess, which is ample, only 0.5 mole of water is formed for each mole of fatty acid on acidification, and this additional amount of water is too small to affect the equilibrium during the esterification to any marked extent. The initial acidity of the fat also contributes to the formation of water, but it will be seen that even in the case of 100% fatty acids interference from this source is not serious.

The fats used were steam-rendered lard, refined peanut oil, soybean oil, and commercial oleic acid. Samples of 100 g. of each fat were refluxed for 1 hr. with 30 g. of potassium hydroxide in 400 ml. of methanol. To the soap solution were added slowly 32 g. of sulphuric acid dissolved in 100 ml. of methanol. This amount of acid is sufficient to neutralize the alkali and to provide 1% (w/v) of free sulphuric acid with regard to methanol. After the addition of some porous clay chips the mixture was refluxed for another hour, whereupon 2.5 g. of anhydrous sodium carbonate were added to neutralize about half of the free sulphuric acid. Two-thirds of the alcohol were distilled off. This partial recovery of methanol is, of course, optional. Then 500 ml. of water were added, and the methyl esters were extracted with two successive 250-ml. portions of ethyl ether. The ethereal extracts were washed with 100 ml. of 10% potassium carbonate solution and afterwards with water. From the alkaline washings the fatty acids were recovered by acidification and extraction with ethyl ether. After distilling off the solvent, both methyl esters and recovered fatty acids were dried *in vacuo* and weighed separately. The free fatty acid content of the methyl esters, estimated as usual, was in all cases below 0.1%.

To compare the above method with the conventional procedure 100-g. samples of fats were saponified with ethanolic potassium hydroxide. The fatty acids were separated as usual and refluxed for two hours with five volumes of methanol containing 1% sulphuric acid. No alcohol was recovered. Table I shows that there was little difference in the yields obtained with either method. It appears therefore that, unless the isolation of fatty acids from the soaps is required for some specific purpose, such as separation into solids and liquids, the *in situ* conversion of soaps into methyl esters saves time and solvents without affecting the final results.

TABLE I

Yields of Methyl Esters and Recovered Fatty Acids Expressed as Percentage of Fats Employed

Sample	Conventional procedure		Direct conversion of soaps	
	% Esters	% Fatty acids	% Esters	% Fatty acids
Lard	99.1	0.8	98.8	1.2
Peanut oil	99.3	0.6	99.1	0.7
Soybean oil	99.2	0.6	99.2	0.9
Oleic acid	104.4	0.5	103.0	1.4

REFERENCES

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2. Youngs, C. G., and Craig, B. M., J. Am. Oil Chemists' Soc., *28*, 521–522 (1951).

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ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

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Application of thermal diffusion to separation of aliphatic alcohols and fatty acids from their mixtures. C. W. Blessin, C. B. Kretschmer and Richard Wiebe (U. S. Dept. of Ag., Peoria, Ill.). *Anal. Chem.* 29, 408–409 (1957). Very little separation by thermal diffusion occurs in binary mixtures of lower aliphatic alcohols or fatty acids. This is attributed to hydrogen bonding, which obscures structural differences and prevents separation.

Synthesis of lanosterol in vivo. P. B. Schneider, R. B. Clayton, and K. Bloch (Harvard Univ., Cambridge, Mass.). *J. Biol. Chem* *224*, 175–183 (1957). Acetate-C^{14} was injected into rats and the animals were killed 10 or 75 minutes later. The unsaponifiable fractions of the intestines and of the liver were analyzed by chromatography and found to contain squalene and lanosterol of high specific activity. Under the same conditions the presence of an intermediate in the conversion of lanosterol to cholesterol can be demonstrated.

Polarographic determination of antioxidants in gasoline. V. F. Gaylor, A. L. Conrad, and J. H. Landerl (Standard Oil Co., Cleveland 6, Ohio). *Anal. Chem.* 29, 228–231 (1957). Antioxidants in gasoline may be determined directly by polarography by measuring the oxidation waves at a wax-impregnated graphite electrode. Lithium chloride in isopropyl alcohol is used as the solvent-electrolyte. A single sample can be analyzed in 45 minutes. Standard deviation of the method is approximately 9%.

Directed interesterification of lard. C. Placek (Associate Editor) and G. W. Holman (The Procter & Gamble Co., Cincinnati, Ohio). *Ind. Eng. Chem.* 49, 162–169 (1957). Directed interesterification of lard is a solution to the plastic-range problem of lard. The process increases the fraction of high melting