

**Employment of ethanol as a solvent in small scale
catalytic hydrogenations of methyl esters**

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ATTENTION HAS BEEN drawn (1) to the possibility of trans-
esterification yielding ethyl esters of fatty acids during

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the hydrogenation of methyl esters when employing ethanol as a solvent. This observation was made with Adams' platinum oxide catalyst and the difficulty could be overcome by using methanol as the hydrogenation solvent. Ethanol, however, in addition to being non-toxic, is also a better solvent at normal temperatures for the higher saturated esters such as methyl stearate (2).

We wish to report that platinum oxide on silicic acid, prepared by the procedure of F. A. Vandenhevel (3), does not lead to transesterification when employed with 95% ethanol in the catalytic hydrogenation of fatty acid esters. This was demonstrated with a freshly prepared lot of catalyst, and also with samples respectively 2 and 3 years old. The latter, although not as active as freshly prepared catalyst, are normally satisfactorily employed in an appropriate hydrogenation apparatus (4) in routine work in this laboratory.

The influence of recovery procedure on the proportion of esters of various chain lengths has also been investigated. Temperatures below 40° have been recommended during vacuum stripping of ethanolic solutions of fatty acid esters (5), presumably to avoid unequal losses of acids of various chain lengths. We have found (Table 1) that with a rotary evaporator disproportionate losses of methyl palmitate and myristate, relative to methyl stearate, are low even when temperatures of 65–75° are employed to speed up vacuum stripping. By any recovery procedure, however, losses of methyl laurate may be appreciable. It is evident that, for procedures employing similar amounts of solvent, particular care must be taken with small samples.

All solvents were distilled before use. Gas-liquid chromatographic analyses were carried out with columns of stainless steel tubing 6 ft in length and 1/8 in. o.d., packed with 5% SE-30 supported on 70–80 mesh Anakrom ABS. The apparatus was based essentially on a Wilkens flame ionization detector. Peak areas were measured by a pipping-pen integrator.

Complete hydrogenations were carried out in ethanol on pure methyl oleate (Hormel Institute) and also with pure methyl palmitate, in both cases employing samples of the order of both 0.2 and 0.05 g (*a* and *b*, Table 1), with different catalysts as discussed above. No ethyl

esters could be detected in the products under analytical conditions such that 0.1% of added authentic ethyl stearate and palmitate were readily recognized.

To ensure complete removal of catalyst and support and a high recovery of esters the following procedure is recommended. The normal analytical hydrogenation procedure is followed (3, 4), although only the bottom edge of the 34/45 cell joint should be greased to avoid contamination of the sample. After hydrogenation, the solution is decanted carefully and the cell and stirrer are rinsed with ethanol. The combined ethanol solutions are then filtered with gentle suction on a small Buchner funnel to remove the bulk of the catalyst and support. A few milliliters of warm ethanol serve as a rinse. A small amount of "fines" may remain in suspension and interfere in some cases with further work. Following removal of the ethanol (preferably on a rotary evaporator), these may be eliminated by taking up the methyl esters in light petroleum ether and centrifuging. This step does not work as well in ethanol and is conveniently carried out at this stage since the esters are normally removed from the distillation flask in petroleum ether for analysis or recovery.

To investigate the possible disproportionate losses of esters during removal of the 95% ethanol, three procedures were examined with a known mixture of esters, again with samples of two different sizes in each case. In the first procedure, the esters were stripped of ethanol (ca. 50 ml) employing a conventional all-glass distillation assembly fitted with a fine capillary bubbler (nitrogen). Full aspirator vacuum was applied and the flask was heated on a steam bath. In the second procedure, a rotary evaporator was employed, again with full aspirator vacuum. Removal of the ethanol was rapid and convenient when the flask was heated on a water bath at 65–75°. In the third procedure, the ethanol solution of the esters was added to 150 ml of water and continuously extracted overnight with Iosol 1520. The Iosol solution was then blown down with nitrogen prior to analysis.

The composition of the recovered methyl ester mixtures is given in Table 1. Weight recoveries exceeded 95% except in the case of the smaller sample subjected to liquid-liquid extraction, where recovery was only

TABLE 1. COMPOSITION OF METHYL ESTER MIXTURE FOLLOWING RECOVERY FROM 95% ETHANOL BY VARIOUS PROCEDURES, EXPRESSED RELATIVE TO COMPOSITION OF STARTING MATERIAL (RECOVERY OF STEARATE TAKEN TO BE 100%)

Ester	Vacuum Stripping					
	Nitrogen Capillary		Rotary Evaporator		Liquid-Liquid Extraction	
	(a)	(b)	(a)	(b)	(a)	(b)
Myristate	90.3	86.9	98.2	93.5	95.5	89.5
Palmitate	98.5	91.0	100.0	98.5	97.3	95.6
Stearate	100	100	100	100	100	100

92.8%. Examination of the ethanol distillates in the first two procedures, and of the extracted solutions in the third, showed recoveries of methyl myristate comparable to the losses relative to recovered stearate. Methyl palmitate could not be detected under the conditions employed. In preliminary experiments involving a similar mixture including methyl laurate, very high losses of methyl laurate were observed in all cases; but since this peak was a shoulder on the solvent curve, accurate estimation was not possible.

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