

PROTECTION OF UNSATURATION DURING HETEROGENEOUS CATALYTIC  
HYDROGENATION OF ALIPHATIC EPOXY TO HYDROXY GROUPS

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When partly-epoxidised fatty esters or glycerides, carrying residual unsaturation, are hydrogenated to the corresponding monohydroxy products at low pressures over a palladium-on-carbon catalyst in an alcohol medium, the presence of silver nitrate in solution has been found to offer complete protection to the ethenoid linkages, probably by  $\pi$ -complex formation.

The epoxy materials were prepared by partial peracetic acid epoxidation of methyl oleate and linoleate, and of groundnut, safflower and linseed oils using a preformed epoxidation reagent (1). In a typical experiment, a methyl linoleate concentrate (I.V. 85) was epoxidised for 3 hr. with 0.6 mole of peracetic acid, poured into cold water, and the partially-epoxidised ester isolated with ether (I.V. 31, oxirane oxygen by HBr titration 3.2 %). To this ester (5 g) was added a solution of silver nitrate (1.7 g) in absolute methanol (75 ml), followed immediately by hydrogenation over 10 % palladium-on-carbon (0.5 g) in a laboratory shaker hydrogenator at room temperature and 30 p.s.i. pressure

for 24 hr. The contents were then filtered, diluted with water, extracted with ether and washed with 2 % hydrochloric acid (500 ml, 5 portions) to give a product of I.V. 32, oxirane oxygen 0.08 % and hydroxyl value (H.V.) 129.

Thin-layer chromatography (2) on silica gel G using ether-light petroleum (20:80 v/v) solvent system showed the presence mainly of non-oxygenated and monohydroxy esters, with traces of residual epoxy and dihydroxy esters.

Trials with various fatty esters and refined vegetable oils are summarised in Table 1. The quantity of silver nitrate used was in slight excess over that calculated from the unsaturation desired to be protected.

TABLE 1

Hydrogenation of partly-epoxidised esters and vegetable oils in the presence of alcoholic silver nitrate

Raw material		Epoxidised product		Hydrogenated product		
Product	I.V.	I.V.	% epoxy	I.V.	% epoxy	H.V.
Methyl oleate	85	31	3.2	32	0.08	129
Methyl linoleate	154	56	5.2	61	0.10	145
Groundnut oil	91	43	2.8	45	0.20	93
Safflower oil	131	54	4.1	60	0.15	134
Linseed oil	185	97	5.0	99	0.12	165

Preliminary experiments had shown that:

a) hydrogenation could be performed soon after addition of silver nitrate, and prior shaking or stirring

of the latter with the ester was not necessary;

b) leaving the partly-epoxidised material in contact with methanolic silver nitrate for 24 hr did not affect the epoxy function; and

c) absolute ethanol is preferable to methanol as medium when epoxidised glycerides are to be hydrogenated, though for esters either is satisfactory.

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