• *Short Communication*

Protection of Unsaturation by Cupric Nitrate During Heterogeneous Catalytic Hydrogenation of Aliphatic Epoxy to Hydroxy Groups

WE HAVE PREVIOUSLY REPORTED (1) that the presence of silver nitrate leads to complete protection of residual ethenoid unsaturation during the catalytic hydrogenation of partly epoxidized unsaturated fatty esters or glycerides to the corresponding monohydroxy products over palladium-on-carbon catalyst in 95% ethanol medium at 30 psi hydrogen pressure. We have now observed that cupric nitrate likewise functions as a protecting agent during hydrogenation under similar conditions except for the use of absolute instead of 95% ethanol as the solvent medium. One mole of cupric nitrate was used for every molar double bond; thus 5 g of partly epoxidized methyl oleate (IV 35.7) required 2.3 g of cupric nitrate trihydrate. Table I shows the results of such hydrogenations.

Thin-layer chromatography on Silica Gel G (2) of partially epoxidized methyl oleate, after such hydrogenation, showed the presence of the expected oleate and monohydroxy esters, accompanied by traces of residual epoxy and of dihydroxy esters resulting from hydration of the epoxy ring.

The presence of palladium chloride during hydrogenation resulted in total ring opening, accompanied however by complete saturation. The use of zinc chloride completely protected unsaturation, but the epoxy ring opening was incomplete even after hydrogenation for 15 hr. Cuprous chloride also protected unsaturation, but thin-layer chromatography showed that chlorohydrins had been formed by reaction of the epoxy ring with hydrogen chloride. Table II shows the results.

TABLE I

Hydrogenation of Partly Epoxidized Esters and Vegetable Oils in the Presence of Alcoholic Cupric Nitrate

Raw material		Epoxidized product		Hydrogenated product		
Product	IV	IV	% epoxy	IV	% epoxy	HV
Methyl oleate	85	35.7	2.8	36.2	0.05	115
Peanut oil	90	43.0	2.9	44.0	0.10	98
Safflower oil	135	52.5	4.3	55.2	0.20	128
Linseed oil	182	99.0	4.8	100.0	0.19	170

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TABLE II

Use of Other Complexing Agents During Hydrogenation

Material used for hydrogenation	Before hydrogenation		Protecting agent used	After hydrogenation		
	IV	% epoxy	mol/mol (oil:agent)	IV	% epoxy	HV
Partly epoxidized methyl oleate	35.7	2.8	$PdCl_2$ (0.5 mol/1 mol)	Nil	Nil	115
Partly epoxidized methyl oleate	35.7	2.8	$PdCl_2$ (1 mol/1 mol)	Nil	Nil	112
Partly epoxidized methyl oleate	35.7	2.8	Cu_2Cl_2 (1 mol/1 mol)	36.2	0.2	110
Partly epoxidized linseed oil	99.0	4.8	$ZnCl_2$ (1 mol/1 mol)	98.9	2.7	76

• *Addendum*

Search for New Industrial Oils. XI. Oils of Boraginaceae, by Robert Kleiman, F. R. Earle, I. A. Wolff, Northern Regional Research Laboratory,[1] Peoria, Illinois, and Quentin Jones, Crops Research Division,[2] Beltsville, Maryland.

Among the data reported under the above title in JAOCS *41*, 459–460 (1964), the sample reported as *Lithospermum officinale* L. has been reidentified as *Heliotropium europaeum* L. Oil from *Moltkia aurea* Boiss. contains 6% of 18:4 instead of 16%. Oil from *Cryptantha bradburiana* Payson contains no 22:1, but 2% of 20:2.

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