SHORT COMMUNICATION

Hydrogenation of Unsaturated Fatty Acid Methyl Esters with Diimide from Hydroxylamine-Ethyl Acetate

A. Gangadhar, T. Chandrasekhara Rao, R. Subbarao and **G. Lakshminarayana***
Regional Research Laboratory, CSIR, Hyderabad-500007, India.

Methyl esters of 10-undecenoic, oleic, linoleic and castor oil fatty acids were hydrogenated with hydroxylamine-ethyl acetate reagent under nitrogen, without change in position and configuration of double bonds. The fatty acid ester was also found to participate in the generation of diimide. No hydrazide was formed.

The position of double bonds in polyunsaturated fatty acids is often determined by partial hydrogenation with hydrazine without affecting the position or configuration of double bonds followed by isolation of monoenes as methyl esters and analysis by either mass spectrometry of their derivatives or by gas-liquid chromatography (GLC) of their oxidation fragments (1). The reduction with hydrazine requires oxygen or oxidizing agents (2). We have already shown (3) that diimide generated *in situ* from hydroxylamine-ethyl acetate is a useful alternative to hydrazine, with the advantage of not requiring oxygen, for hydrogenation of a variety of unsaturated fatty acids. Reduction with hydrazine is not normally done on fatty acid methyl esters (FAME) because of the formation of hydrazides (4). In the present work, we show that hydroxylamine-ethyl acetate can also be used for the reduction of FAME without the formation of hydrazides as byproducts.

EXPERIMENTAL

The materials and methods used were the same as reported earlier (3).

Partial hydrogenation of FAME was carried out according to the procedure described in our earlier communication (3). The reagent solution prepared by mixing ethyl acetate and hydroxylamine—which was freshly liberated from hydroxylamine-hydrochloride with powdered potassium hydroxide in dimethylformamide (DMF)—was added to the unsaturated FAME during 1.5 hr at 90-95°C under nitrogen. After heating the mixture for an additional hour, the product was worked up as described earlier (3). The acid value (AV) of the total product was determined and the product was esterified using diazomethane in methanol. The monoenoates and saturated esters were isolated by preparative thin layer chromatography (TLC) on Silica gel G impregnated with silver nitrate. The monoenoates were derivatized to the corresponding methoxyderivatives by methoxymercuration-demercuration procedure (5). The methoxyderivatives thus obtained were purified by preparative Silica gel G TLC and subjected to mass spectral analysis (6).

In order to ascertain whether the FAME itself participates in the generation of diimide as does ethyl acetate, an experiment using methyl 10-undecenoate was carried out without ethyl acetate. The product was analyzed for AV and extent of hydrogenation by GLC.

TABLE 1

Hydrogenation of Unsaturated Fatty Acid Methyl Esters with Hydroxylamine-Ethyl Acetate

Ester	Purity/ composition (wt%)[a]	Acid value	Product/ composition (wt%)[a]		Acid value
10-Undecenoate	98.9	0.3	Methyl undecanoate	63.6	14.0
			Methyl 10-undecenoate	35.3	
Oleate	99.5	0.1	Methyl stearate	56.8	12.8
			Methyl oleate	43.2	
Linoleate	99.7	0.2	Methyl stearate	26.0	10.5
			Isomeric methyl oleates	50.5	
			Methyl linoleate	23.2	
Castor FAME		0.3			24.1
16:0	2.0		16:0	2.2	
18:0	2.0		18:0	5.6	
18:1	3.0		18:1	3.2	
18:2	3.0		18:2	1.1	
18:1 (OH)	90.0		18:0 (OH)	54.5	
			18:1 (OH)	33.4	

[a]By gas chromatography.

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*To whom correspondence should be addressed.

RESULTS AND DISCUSSION

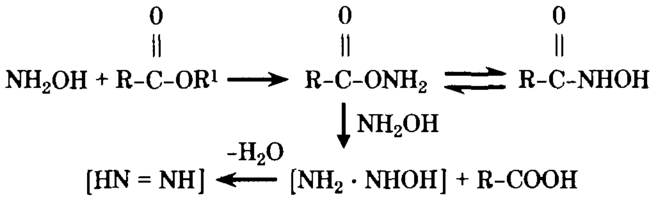
The composition of the starting FAME, as well as the hydrogenated products, are given in Table 1. A comparison of the AV of starting FAME and the corresponding hydrogenated products indicated the presence of free fatty acids. To ascertain the origin of free fatty acids, methyl undecenoate was used as substrate as well as a substitute for ethyl acetate. The product had an AV of 10.7. After esterification of the free fatty acids with diazomethane, the GLC analysis of the total product showed it to contain 17% undecanoate and 83% undecenoate. These results show that the FAME contributes to the generation of diimide from hydroxylamine (Scheme 1) during the diimide reduction.

The IR spectra of the partially hydrogenated FAME showed no *trans* unsaturation, indicating that the hydrogenation was stereospecific. Silver ion TLC of partially hydrogenated methyl linoleate gave only *cis*-monoenoates which were shown to be a mixture of only 9- and 12- isomers by mass spectrometry of their methoxyderivatives (5,6), indicating no migration of double bonds.

Disproportion of unreacted diimide may result either in the formation of hydrazine or nitrogen and hydrogen. It is well known that FAME react with hydrazine and form high-melting hydrazides (4,7). Therefore, the hydrogenated products were analyzed for the presence of hydrazides by various physical and chemical techniques. Silver ion TLC showed only two bands corresponding to saturated and unsaturated FAME. The melting points of the saturated bands separated from the total products of methyl oleate and methyl linoleate were 38.9°C and 38.6°C, respectively, indicating that the saturated bands contain only methyl stearate (m.p. 39.1°C) and no stearic acid hydrazide, (m.p. 115.6-116.2°C) (4). The IR spectra of hydrogenated FAME showed no characteristic absorptions for hydrazide at 3310 cm^{-1} (N-H stretching) and at 1625 cm^{-1} (CO stretching), which ruled out the possibility of formation of hydrazides.

Unlike hydrazine, hydroxylamine-ethyl acetate reagent is less toxic and can be used for structure determination through partial hydrogenation of either unsaturated fatty acids or FAME in the absence of oxygen or oxidizing agent.

Scheme 1



$$NH_2OH + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR^1 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}ONH_2 \rightleftharpoons R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NHOH$$

$$\downarrow NH_2OH$$

$$[HN = NH] \xleftarrow{-H_2O} [NH_2 \cdot NHOH] + R\text{-}COOH$$

$R = CH_3$ or Fatty acid chain ; $R^1 = CH_3$ or C_2H_5

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