Stereospecific Hydrogenation of Stearolate With Copper Catalysts

Unsaturated fatty acids are generally synthesized from their corresponding acetylenic acids (1,2). Hydrogenation of the triple bond to *cis* double bond is accomplished with poisoned catalysts (1,3) and with Raney nickel (2). Some saturates are usually formed with these catalysts. We have found that copper catalysts reduce triple bonds to *cis* monoenes. Since these catalysts do not hydrogenate monoenes (4), the product obtained is free from saturates.

Hydrogenations were carried out at 150C and atmospheric hydrogen pressure in an all glass manometric apparatus (5) with three different copper catalysts. Methyl stearolate (0.5 ml) was hydrogenated in the presence of 50 mg of copper chromite, copper-barium chromite or 10% copper-on-Cab-O-Sil (6). When the rate of hydrogen uptake was negilgible, the hydrogenated product was separated from the catalyst by filtration and distilled under vacuum. GLC analysis indicated that 96% to 99% of the stearolate was reduced to monoene. Infrared analysis showed no *trans* bonds. Oxidative ozonolysis of the hydrogenated product showed that the double bond was at the 9 position.

We have also found that the triple bond in stearolate is preferentially reduced over the double bonds in linoleate. Thus, it would appear that *cis* polyunsaturated fatty acids can be prepared with copper catalysts from polyacetylenic acids.

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Volatile Products From Autoxidized Methyl Linoleate: Comparison at Peroxide Levels of 100-150 and 1000

IN AN EARLIER STUDY of oxidizing methyl linoleate to a peroxide value (PV) of 1,000 mmole/kg (1), we found acyclic acetals and 2,4-dialkyldioxolanes, which were thought to be formed via secondary reactions that consumed free aldehydes. We felt that by decreasing oxidation time these secondary reactions would be minimized. We ran additional experiments in which the original oxidation and analytical procedures were modified. The two principal modifications were: purified oxygen was maintained at an approximately constant pressure over the dispersed methyl linoleate instead of passing oxygen at a low flow rate through the sample of dispersed ester; and, for isolating the volatile fraction, vacuum distillation was substituted for trapping the volatiles from the effluent oxygen stream in cold traps at −80 C. It was found that vacuum distillation was 25–35 times more efficient (based on the volume of material obtained from both techniques from the same weight of ester) than the sweeping technique previously used. Also, GLC analysis of these volatile fractions from both techniques showed no qualitative differences.

Methyl linoleate (45 g, 97% as analyzed by gas-liquid chromatography, PV < 1, prepared from fresh pressed safflower oil by the method of Swern and Parker (2), all isolation procedures conducted under a nitrogen blanket) was oxidized on purified glass wool at room temperature (22 C) for 7 to 9 days, which was needed to provide enough volatile material for gas chromatographic-mass spectral analysis. After this time, it had a PV of 100–150 mmole/kg. During the oxidation, purified oxygen (passed through a filter containing activated alumina, charcoal and Linde type 5A molecular sieve) was maintained at an approximate pressure of 855 mm over the methyl linoleate.

Volatile products from the oxidation were vacuum-transferred into a U-tube, where two phases were formed. The smaller, upper organic phase was analyzed on a 200-ft, 0.01-in. gas chromatographic column coated with General Electric SF 96(50) silicone oil containing 5% Igepal CO-880. The rest of the combined mass spectrometry-gas chromatography (MS-GC) procedure was the same as before (1).

In order to minimize the introduction of artifacts all the glassware used in these experiments was washed with concentrated nitric acid and rinsed with

TABLE I
Comparison of Volatile Compounds from Autoxidized Methyl Linoleate at PV 100–150 and PV 1000[a] mmol/kg

Compounds[b]	PV 100–150	PV 1,000
carbon dioxide	+	+
methyl formate	+	+
pentane	+	+
acetone	+	0[c]
butanal	+	+
2-methyltetrahydrofuran	+	—
2-pentanone	+	+
pentanal	+	+
hexanal	+	+
amyl formate	+	+
2-heptanone	+	+
methyl hexanoate	+	+
1,1-dimethoxyhexane	—	+
2-heptenal	+	+
methyl heptanoate	+	+
2-octenal	+	+
methyl octanoate	+	+
2-ethyl-4-pentyldioxolane	—	+
geometric isomer of 2-ethyl-4-pentyldioxolane	—	+
pentyl hexanoate	+	+
1-methoxy-1-pentoxyhexane	—	+
2-propyl-4-pentyldioxolane	—	+
geometric isomer of 2-propyl-4-pentyldioxolane	—	+
2-butyl-4-pentyldioxolane	—	+
geometric isomer of 2-butyl-4-pentyldioxolane	—	+
cis-2,4-dipentyldioxolane	—	+
trans-2,4-dipentyldioxolane	—	+

[a] Compounds previously identified from autoxidized methyl linoleate, PV 1,000 (1).
[b] Compounds identified in low and high level oxidations are listed in order of increasing GLC retention times.
[c] Not identified, but could be present in very low levels and not be identified by the GC-MS technique used. (GC retention times of acetone and pentane are similar.)

distilled water. The glass wool used was purified by extensive washings with carbon tetrachloride followed by distilled water and then dried in a vacuum desiccator. Gas-liquid chromatographic analysis of headspace gas samples (5–15 ml) from the purified glass wool using a gas chromatograph equipped with a flame ionization detector showed the absence of volatile compounds. Also, blanks were run consisting of purified glass wool exposed to oxygen for seven to nine days and then vacuum distilled at ambient temperature at 20–60 μ. Only a trace of water (estimated volume < 20 μl) was obtained.

Table I contains a comparison of the volatile compounds identified from autoxidized methyl linoleate at peroxide levels of 100–150 and those obtained previously at PV of 1,000 mmole/kg. Each listed compound was identified by comparison of its gas chromatographic and mass spectral data with those of an authentic compound.

2-Methyltetrahydrofuran was found in the less oxidized system but not in the more highly oxidized system. However, this compound could be either absent or present in a low level in the more highly oxidized system since it might not separate from the larger amount of 2-pentanone, as the GLC retention times of the two are close. Identification of 2-methyltetrahydrofuran by means of our MS-GC technique in an abundance of 2-pentanone would be impossible due to the similarities of the mass spectral features of these compounds.

The mechanism of formation of 2-methyltetrahydrofuran is not known. Tetrahydrofurans have been reported to be formed by oxidation of hydrocarbons (2), (3)–specifically 2-methyltetrahydrofuran from pentane (4) but at temperatures above 300 C.

1,1-Dimethoxyhexane, 1-methoxy-1-pentoxyhexane and 2,4-dialkyldioxolanes were shown to be absent in the more mildly oxidized system (Table I) by the MS-GS technique employed. This finding of the absence of these compounds is consistent with our hypothesis that certain secondary reactions consuming aldehydes are responsible for 2,4-dialkyldioxolanes and acetals.

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Nature of Residual Lipids in Menhaden Fish Protein Concentrate

RECENTLY WE DESCRIBED the residual lipids of a fish protein concentrate (FPC) prepared from red hake (*Urophycis chuss*) (1). Hake is a relatively low-fat fish. However, most of the fish that could be utilized for FPC are high in fat; hence we have now analyzed the residual lipids in an FPC prepared from menhaden, a fatty fish. Menhaden (*Brevoortia tyrannus*) has been used for many years in the manufacture of fish meal. FPC was made from fresh menhaden fish by extraction with 2-propanol in the laboratory glassware unit (2) (Bureau of Commercial Fisheries at College Park, Maryland) and furnished to us as batch M-3. The residual lipids were extracted and analyzed by the methods previously used except that non-lipid contaminants were removed by Sephadex chromatography (3).

The menhaden FPC, M-3, was found to have approximately the same amount of residual lipid (chloroform-soluble material) as did the hake FPC, batch GO-1 (Table I). Thin-layer chromatography (TLC) showed that the menhaden lipid was almost

TABLE I
Lipid Content of FPC

Sample	Weight g	Number of days extracted	Yield[a] g	Yield[a] %
GO-1 (hake)	250	14	0.28	0.11
M-3 (menhaden)	250	15	0.38	0.15

[a] The lipids were extracted in a Soxhlet apparatus (chloroform-methanol, 2:1) (2), and the chloroform-soluble material was purified by Sephadex chromatography (3). Aliquots were evaporated to dryness and weighed on a Cahn electrobalance, Model G.