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