The Autoxidation of Linoleates at Elevated Temperatures

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ABSTRACT

To investigate the effects of heating conditions on the decomposition of linoleates, samples of linoleic acid and its esters were heated at 70 C, 180 C and 250 C for different periods of time and their decomposition products analyzed by gas chromatography and mass spectrometry. Qualitatively, the polar decomposition products were basically the same. However at the higher temperature and longer heating time the nonpolar decomposition products contained a large number of cyclic hydrocarbons which could not be detected with the milder heat treatments. A series of alkyl ethers, not previously reported, was identified in samples heated at 250 C for 5 hr. Quantitatively, hexanal and aldehyde esters were found in significantly greater amounts in the samples heated at a lower temperature, whereas the reverse was true for *t,t*-2,4-decadienal.

INTRODUCTION

Unsaturated fatty acids are much more susceptible to oxidation than their saturated analogs. At elevated temperatures their oxidative decomposition proceeds very rapidly. Although certain specific differences between high and low temperature oxidations have been observed by some investigators, the evidence accumulated to date indicates that in both cases the principal reaction pathways are basically the same. The formation and decomposition of hydroperoxide intermediates, predictable according to location of double bonds (1-3), apparently occur over a wide temperature range. A large number of decomposition products has been isolated by many investigators from heated fats (4-6). However, the major compounds are typical of those ordinarily produced from room temperature autoxidation.

This study with linoleates is part of a continuing effort in our laboratory to determine the effects of heating conditions on fat decomposition.

EXPERIMENTAL PROCEDURES

Linoleic acid, ethyl linoleate and propyl linoleate were purchased from Sigma Chemical Co., St. Louis, MO. Each of these compounds was tested for purity by gas chromatography (GC) and found to contain up to 1% oleic acid as the only impurity. One g of fatty acid or fatty acid ester was heated in air in a 200-ml round-bottomed flask at various heating times and temperatures. The volatile decomposition products were recovered by high-vacuum, cold-finger distillation as previously described (7). The cold finger was washed with 20 ml of pentane which was then washed with 5 g of Florisil (Applied Science Laboratories, Inc.). Polar compounds were retained onto the Florisil, whereas nonpolar compounds remained in pentane. The Florisil slurry was placed in a medium-pore Buchner funnel and washed with 10 ml of pentane, which was collected, concentrated under a gentle flow of nitrogen and set aside for further analysis by GC. The Florisil was then washed with 10 ml of anhydrous diethyl ether to yield the polar

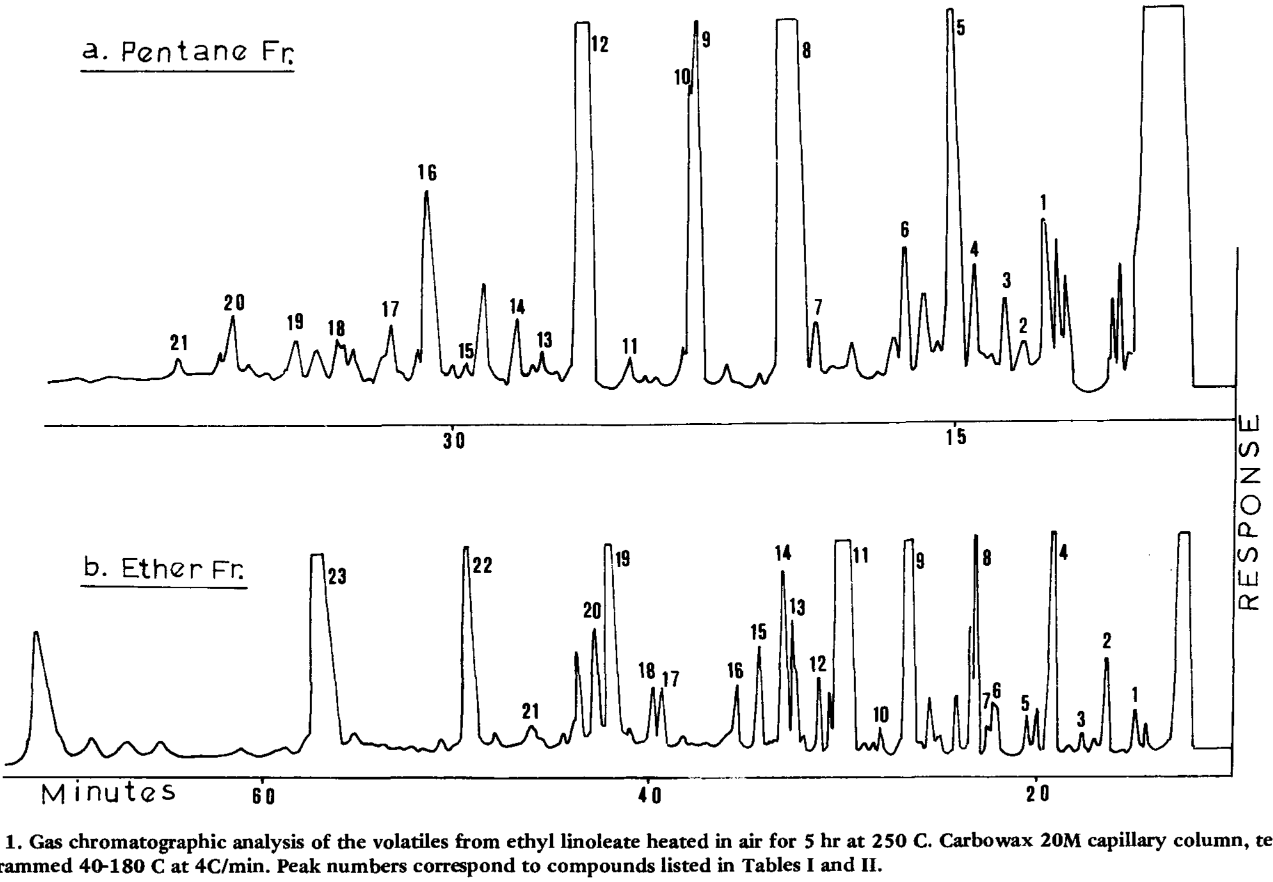

FIG. 1. Gas chromatographic analysis of the volatiles from ethyl linoleate heated in air for 5 hr at 250 C. Carbowax 20M capillary column, temp.-programmed 40-180 C at 4C/min. Peak numbers correspond to compounds listed in Tables I and II.