Identification of 2, 4, 6-Trialkyl-1, 3, 5-Trioxanes from Autoxidized Methyl Linoleate by Mass Spectrometry[1]

ROBERT J. HORVAT, W. H. McFADDEN, H. NG, W. G. LANE and A. D. SHEPHERD
Western Regional Research Laboratory,[2] Albany, California

Abstract

2,4-Dibutyl-6-pentyl-1,3,5-trioxane, 2-butyl-4,6-dipentyl-1,3,5-trioxane, and 2,4,6-tripentyl-1,3,5-trioxane have been identified in the volatile products from autoxidizing methyl linoleate by mass spectrometry. The principal component is 2,4,6-tripentyl-1,3,5-trioxane. These compounds appear to be formed from condensation of hexanal and pentanal, the two major aldehydes in the volatiles from autoxidizing methyl linoleate (5).

Introduction

During a study of the volatiles from autoxidation of methyl linoleate to relatively high peroxide values (1000 millimols/Kg) by GLC analyses, some high-molecular-weight compounds were observed. These compounds were not observed in samples of methyl linoleate with lower peroxide values (100–150 mmoles/kg). Therefore, they appear to be products of secondary reactions. These compounds have not been reported by other investigators studying the autoxidation of methyl linoleate (2) and soybean oil (3).

The identification of these compounds and a possible explanation of their origin is herein reported.

Experimental

Seventy-five grams of methyl linoleate (97% pure as analyzed by GLC, peroxide number negligible) was oxidized as a film on clean glass wool by continuous exposure to purified oxygen (793 mm) at room temperature in laboratory light. After oxidation the ester had a peroxide number of approximately 1000 mmoles/kg. The volatiles from the autoxidized methyl ester were vacuum transferred from the oxidized ester at 25C and a pressure of 10–20 μ mercury and collected in a U-tube at −78C. The 2 to 4 ml of condensate separated into two layers. The lower layer, mostly water, was not analyzed in this study. Appropriate volumes, 40 to 50 μl, of the organic upper layer were chromatographed on a 4-ft × 1/4 in. stainless steel column packed with 20% Apiezon L on Chromosorb P. The column was programmed from 150 to 200C over 30 min. Three major unknown fractions plus the two previously identified isomeric 2,4-dipentyl-1,3-dioxolanes (5) were collected (see Fig. 1). Each of the three unknown fractions showed only one component when analyzed on a 200-ft. × 0.01-in. capillary column coated with General Electric SF 96(50) Silicone Oil. The infrared spectra of these three compounds were similar and showed bands at 1150 cm^{-1} and 1250 cm^{-1}, indicating the presence of C-O bonds.

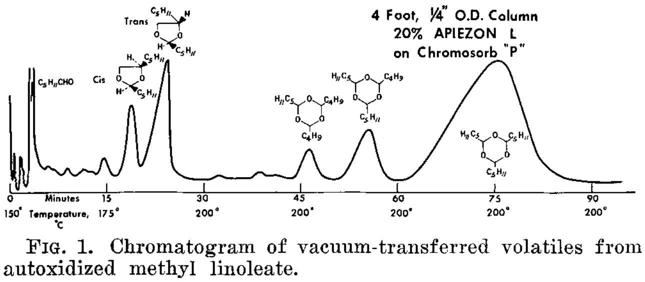

FIG. 1. Chromatogram of vacuum-transferred volatiles from autoxidized methyl linoleate.

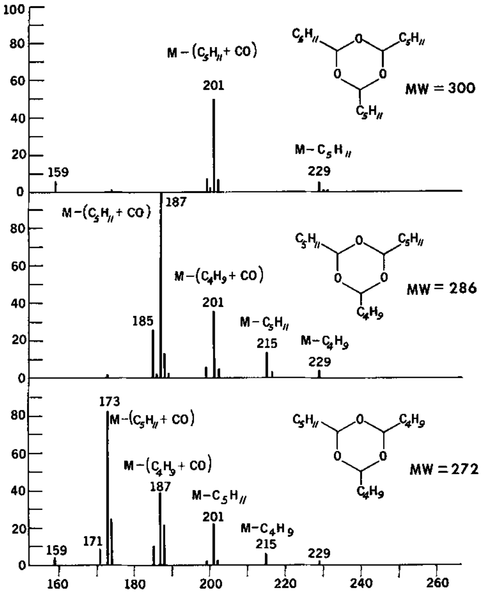

FIG. 2. Mass spectra of trialkyl trioxanes.

The mass spectra of the three compounds showed certain similarities indicating they were members of a homologous series of trialkyl trioxanes. The higher-molecular-weight regions of the mass spectral fragmentation patterns of the trialkyl trioxanes are shown in Figure 2. In the spectrum of 2,4,6-tripentyl trioxane, loss of a single pentyl fragment yields the ion at mass 229 and a more abundant fragment ion is collected at mass 201 corresponding to loss of (C_5H_{11} + CO). In the mass spectra of the pentyl butyl trioxanes, ion currents are observed corresponding to M-C_5H_{11}, M-C_4H_9, M-(C_5H_{11} + CO), and M-(C_4H_9 + CO). These readily permit identification of the specific mixed alkyl system on the trioxane. The ion current collected as the parent ion is low, but in reasonably intense spectra about 0.1% of the ion current is observed at M-1 corresponding to loss of H. The lower-molecular-weight ranges of the spectra were useful only for comparing authentic samples with the unknowns.

Loss of the CO group requires an intramolecular rearrangement whereby a hydrogen is transferred to the other parts of the molecule ion. Whether the fragment due to loss of (R + CO) occurs as loss of R followed by loss of CO or by loss of the fragment R-CO was not determined. Accurate mass determination on a CEC 21-110 double-focusing mass spectrometer established that the ion fragment thus formed contained only two oxygens and the possible loss of C_2H_4 rather than CO need not be considered.

Authentic samples of 2,4-dibutyl-6-pentyl-1,3,5-trioxane and 2-butyl-4,6-dipentyl-1,3,5-trioxane were

---

[1] Presented at the Symposium on Mass Spectrometry Applied to Lipids, AOCS Meeting, Cincinnati, October 1965.
[2] W. Utiliz. Res. Dev. Div., ARS, USDA.

prepared from equimolar quantities of pentanal and hexanal by a modification of the sulfuric acid-catalyzed condensation described by Fieser (4). After the addition of water to the reaction mixture, we extracted the products with ether. The ether solution was washed with dilute sodium bicarbonate, then water, and dried over anhydrous sodium sulfate. Ether and most of the hexanal and pentanal were distilled from the products at a pressure of 20 mm mercury. The desired trioxanes were separated from the reaction products on the same preparative GLC column previously used for separation of the three trioxanes from the distillate of autoxidized methyl linoleate. A quantity of hexanal trimer was also prepared from hexanal alone by the same procedure. The GLC retention times, mass spectra, and infrared spectra of the authentic samples of substituted trioxanes were identical to those of the unknown compounds.

In order to obtain analytical chemical evidence for the structure of the major trialkyl trioxane, 2,4,6-tripentyl-1,3,5-trioxane was hydrolyzed in 3 M hydrochloric acid in 30% methanol in a sealed tube at 110C for 4 hr. The hydrolysis products were extracted with ether and separated by GLC on a Carbowax 20 M column. Two of the three major products were identified as hexanal and 1,1-dimethoxy hexane by mass spectrometry and GLC retention times of the unknown and authentic samples. The third major compound was identified as 2-butyl-2-octenal, the aldol condensation and subsequent dehydration product of hexanal, by comparison of its infrared spectrum and mass spectrum with an authentic sample of this aldehyde. In order to determine whether 1,1-dimethoxy hexane and 2-butyl-2-octenal were artifacts formed from hexanal liberated during hydrolysis of the major trioxane, hexanal was heated under the same hydrolysis conditions. The same two products were identified by identical techniques.

This analytical chemical evidence supports the 2,4,6-tripentyl trioxane structure.

It appears that the substituted trioxanes could be secondary reaction products formed from hexanal and pentanal (5), because it is known that some acids catalyze trimerization of some aldehydes. Since formic acid was previously identified in the acid fraction from autoxidized methyl linoleate (1), we decided to determine whether this acid could catalyze trimerization of hexanal and pentanal.

A catalytic quantity of 97% formic acid was added separately to hexanal (97%) and pentanal (95)%. The two solutions were allowed to stand at room temperature for ten days and then treated as previously described for the preparation of 2-butyl-4,6-dipentyl- and 2,4-dibutyl-6-pentyl-1,3,5-trioxane. Small quantities of 2,4,6-tributyl- and 2,4,6-tripentyl-1,3,5-trioxane were isolated from these two solutions by preparative GLC and their identity confirmed by infrared and mass spectroscopy. To eliminate the possibility that the substituted trioxanes were not already present in the hexanal and pentanal, the same quantities of hexanal and pentanal were concentrated by a rotary evaporator at 20-mm pressure. GLC analysis of this concentrate showed negligible amounts of trioxanes. Therefore it appears reasonable that the substituted trioxanes are secondary products and could form by a formic acid-catalyzed trimerization of hexanal and pentanal.

ACKNOWLEDGMENT

Research supported in part by funds from the Office of Civil Defense, Department of Defense.

REFERENCES

1. Unpublished results from the authors' laboratory.
2. Privett, O. S., and M. L. Blanks, JAOCS *39*, 465–469 (1962).
3. Chang, S. S., K. M. Brobst, H. Tai and C. E. Ireland, JAOCS *38*, 671–674 (1961).
4. Fieser, L. F., and M. Fieser, "Advanced Organic Chemistry," 1st ed., Reinhold Publishing Corporation, 1961, p. 395.
5. Horvat, R. J., W. H. McFadden, H. Ng, D. R. Black, W. G. Lane and R. M. Teeter, JAOCS, *42*, 1113 (1965).