Effect of Thioanisole and Trimethylene Sulfide on the Oxidation and Yellowing of Methyl Linolenate

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The effect of thioanisole and trimethylene sulfide on the autoxidation and yellowing of methyl linolenate has been investigated by nuclear magnetic resonance (NMR) and ultraviolet visible spectroscopy, respectively. The progress of autoxidation was followed by measuring the NMR integration of vinylic protons with respect to methoxy protons, which served as the internal standard, as a function of time. The degree of yellowing was determined by measuring the difference in absorbance at 400 nm and 450 nm as a function of time. Both thioanisole and trimethylene sulfide enhanced the autoxidation of methyl linolenate. Inhibition of yellowing was observed only with trimethylene sulfide.

KEY WORDS: Acceleration, autoxidation, inhibition, methyl linolenate, yellowing.

The autoxidation of fatty esters (RH) is commonly observed in deteriorating foods containing unsaturated fats and in edible oils exposed to air and can be described as given below (1-3):

$$\mathrm{RH} \overset{-\mathrm{H}\cdot}{\rightleftharpoons} \mathrm{R}\cdot \overset{\mathrm{O_2}}{\rightleftharpoons} \mathrm{ROO}\cdot \xrightarrow{\mathrm{RH}} \mathrm{ROOH} + \mathrm{R}\cdot$$

This process often leads to unpleasant odors and flavors of foods and oils due to the generation of volatile decomposition products. However, autoxidation is crucial for fast drying of oil-based paint films. Linseed oil, which has a high content of linolenate undergoes rapid oxidation on exposure to air to form a polymeric film. The yellowing of linseed oil-based paints, particularly in the dark, a process associated with autoxidation, limits the use of linseed oil in indoor paints (4-6). However, exterior paints show less yellowing because of the bleaching of yellow compounds formed during autoxidation by sunlight (7).

The effect of optical brighteners (8), linolenate content (9) and driers (10) on the yellowing of linseed oil-based paints has been studied extensively. Rakoff *et al.* (11) observed ozonized commercial monoolein and acetoacetic ester to show significant inhibition of yellowing of linseed oil-based paints. In our laboratory, we observed that glycerol, glucose and acetoacetoxyethyl methacrylate show significant inhibition of yellowing of methyl linolenate (12). However, no compound has been identified to inhibit yellowing completely. Previous studies on yellowing of methyl linolenate suggested that aldehydes, particularly low-molecular weight aliphatic aldehydes, inhibit yellowing of methyl linolenate (5). We believe that this decrease in yellowing, caused by aldehydes, was due to the chemical reduction of the yellow compounds or precursors of yellow compounds. Therefore, we were interested in looking for organic compounds other than carbonyl compounds that could reduce these colored species efficiently. In our studies, thioethers (sulfides), which are known to react with oxidizing agents readily to produce sulfoxides and sulfones, were investigated. Here, we report the effect of thioanisole (TA) and trimethylene sulfide (TS) on the autoxidation and yellowing of methyl linolenate (ML_3). In this study, the progress of the reaction was followed by ^1H nuclear magnetic resonance (NMR) (12,13), where the disappearance of vinylic protons was measured with time, while using the methoxy protons of methyl linolenate as internal standard.

MATERIALS AND METHODS

Thioanisole, trimethylene sulfide and methyl linolenate were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. The ^1H NMR spectra were obtained on a Bruker (Burlington, Ontario, Canada) EM-300 spectrometer at 300 MHz.

General procedure for autoxidation. In a small test tube (4 mL) equipped with a septum and oxygen inlet (disposable glass pipette) and outlet needle, 223 μL (200 mg) of methyl linolenate was placed under nitrogen. Oxygen was bubbled through the liquid at 45°C (heated in a water bath), at a rate of 20 mL/min in the dark. A fixed volume of sample was taken, under nitrogen, every 5 h for NMR analysis. In the case of ML_3-TA and ML_3-TS systems, 5 mol% of thioanisole and trimethylene sulfide were added to ML_3, respectively.

General procedure for yellowing. Methyl linolenate (34 μL, 30 mg) was spotted on the center of a white Whatman filter paper (4.25-cm diamter) (Maidstone, England). The filter paper was then placed on a glass triangle in a headspace cell with a water jacket at 40°C (this temperature was maintained by circulating heated water from a temperature-controlled water bath with a pump). The cell was coated with black paint to prevent the sample from exposure to light. A stream of air was allowed to flow through the closed headspace. The absorbance of the liquid-absorbed filter paper was measured every 24 h, using a Unicam SP-800 spectrophotometer (Cambridge, England) equipped with a reflectance accessory. In the case of ML_3-TA and ML_3-TS, solutions of the 5 mol% of the corresponding sulfur compound and ML_3 in dichloromethane were spotted separately on filter papers.

RESULTS AND DISCUSSION

Methyl linolenate is known to produce monohydroperoxides (ROOH) at the initial stages of autoxidation. These monohydroperoxides undergo further oxidation with time to form other oxygenated and decomposition products. In our investigation, the disappearance of vinylic protons with respect to methoxy protons, determined by integration values, was plotted against time to study the effect of thioanisole and trimethylene sulfide on the autoxidation of methyl linolenate. Autoxidation of ML_3-TA and ML_3-TS systems was slightly faster than for ML_3 in the initial stages of autoxidation (Fig. 1). A similar type of prooxidative effect of sulfides was observed in the autoxidation of tetralin by Scott (14). We believe that this prooxidative effect of sulfide may have been caused by the reaction of sulfides with peroxy radical to produce alkoxy

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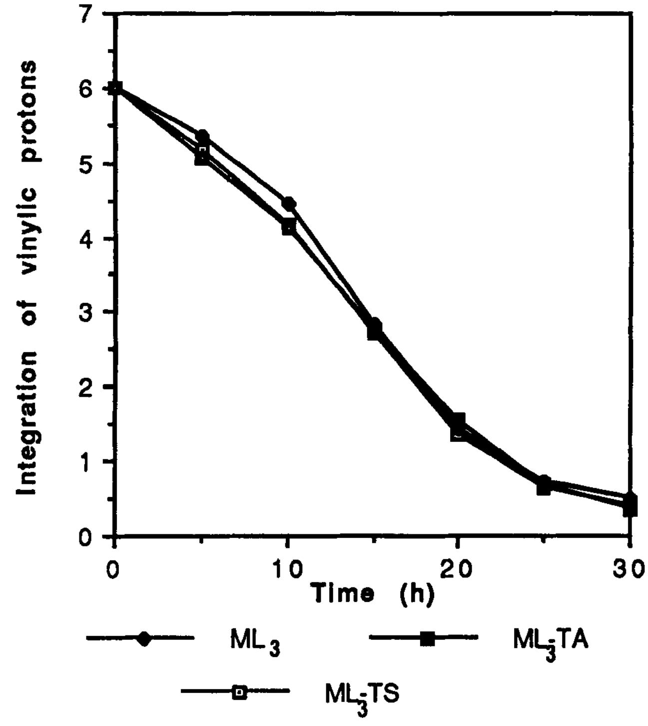

FIG. 1. The effect of thioanisole (TA) and trimethylene sulfide (TS) on autoxidation of methyl linolenate (ML$_3$).

radicals and sulfoxides. This behavior of sulfides is comparable to the prooxidative effect of aldehydes (5,12) and, therefore, could be following the same mechanism in influencing the autoxidation of unsaturated fatty esters.

The yellowing studies were carried out with films (liquid absorbed on paper) of these systems, by measuring the difference at 400 nm and 450 nm (400–450 nm is the blue region of visible light in which yellow compounds absorb strongly):

$$\text{degree of yellowing} = (A_{400}\text{-}A_{450})_t - (A_{400}\text{-}A_{450})_o = \Delta \quad [1]$$

where $(A_{400}\text{-}A_{450})_t$ = difference in the absorbance at 400 nm and 450 nm at time t, and $(A_{400}\text{-}A_{450})_o$ = difference in the absorbance at 400 nm and 450 nm at time t = 0, which was negligible for all systems.

Detectable inhibition of yellowing was observed with ML$_3$-TS but not with ML$_3$-TA (Fig. 2). This inhibition by trimethylene sulfide may be caused by the chemical reduction of yellow compounds or of precursors of yellow compounds. The limited solubility of trimethylene sulfide in methyl linolenate limits its use in the inhibition of yellowing. Difference in behavior of thioanisole could be due to the presence of an aromatic group. This is similar to the observation reported by Privett *et al.* (5), where aliphatic aldehydes were observed to inhibit yellowing, but aromatic aldehydes were not effective. These results suggest that organic compounds other than carbonyl compounds with reducing functionality might be utilized in the inhibition of yellowing. We are currently investigating the possible use of other thioethers with one or more sulfide units for the prevention of yellowing. The mechanism by which these compounds influence autoxidation and yellowing is also under investigation.

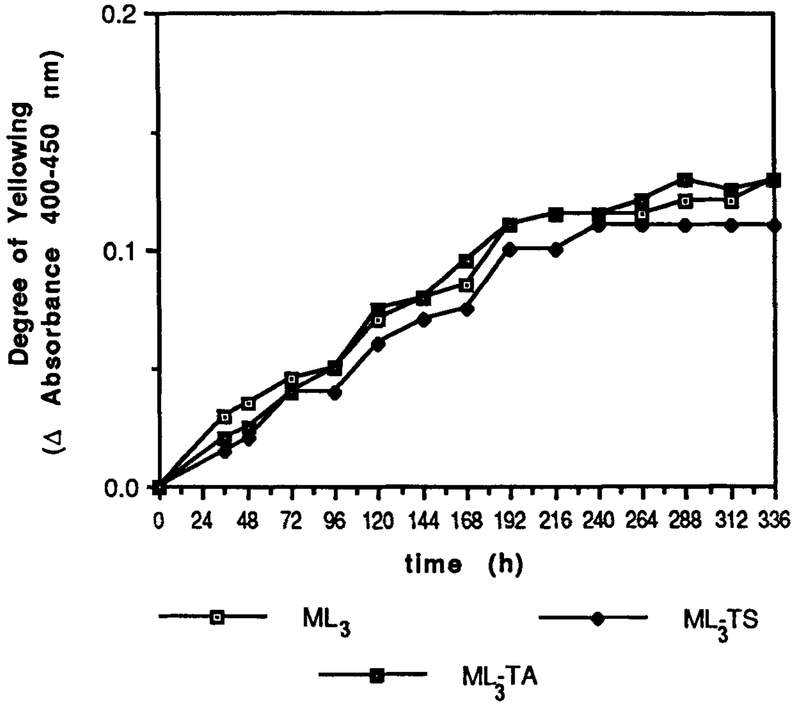

FIG. 2. The effect of thioanisole (TA) and trimethylene sulfide (TS) on yellowing of methyl linolenate (ML$_3$).

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