Glycerol, Glucose and 2-Acetoacetoxyethyl Methacrylate: Effect on Methyl Linolenate Oxidation and Yellowing

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The effect of glycerol, glucose and acetoacetoxyethyl methacrylate (AAEM) on autoxidation and yellowing of methyl linolenate has been investigated by nuclear magnetic resonance (NMR) and ultraviolet (UV)-Visible spectroscopies. The extent of autoxidation was determined by measuring the NMR integration of vinylic protons with respect to methoxy protons, an internal standard, as a function of time. The extent of yellowing was determined by measuring the difference in absorbance at 400 nm and 450 nm as a function of time. Glycerol and AAEM showed inhibition of autoxidation, but the most significant effect was observed with AAEM. Glucose enhanced the autoxidation of methyl linolenate. Inhibition of yellowing was observed with all these compounds, especially with glycerol and AAEM.

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

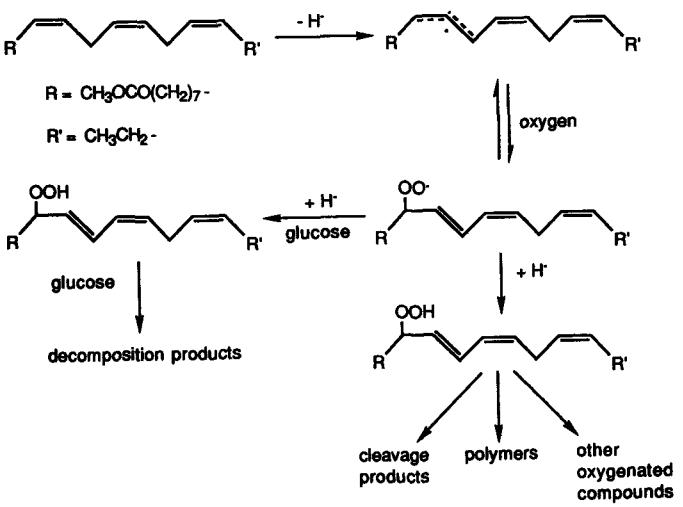
Autoxidation of fatty esters has been an important topic and is studied extensively in order to understand the deterioration of foods containing unsaturated lipids (1–3). The mechanism of this process has been investigated and is well understood for simple fatty esters, such as oleate, linoleate and linolenate, because it is less complicated than for triglycerides. Linseed oil, which contains these unsaturated fatty acids, predominantly linolenic acid, is often used in the paint industry as a drying oil. Linolenic acid, with three methylene-interrupted double bonds, undergoes autoxidation to form a dry polymeric film (Scheme 1) faster than do oleate and linoleate with one and two double bonds, respectively. However, the presence of a high content of linolenate in linseed oil makes linseed oil-based paints less desirable for indoor painting due to the tendency for yellowing of these paints during autoxidation, particularly in the dark (4–6). Exterior paints show less yellowing because the yellow compounds formed during autoxidation are bleached by sunlight (7).

Rakoff *et al.* (8) studied the effect of driers, linolenate content (9) and optical brighteners (10) on the yellowing of linseed oil-based paints. They determined that ozonized commercial mono-olein and acetoacetic ester inhibit yellowing significantly (11). However, neither the compound that causes yellowing nor a method to provide complete inhibition of yellowing is known at present.

Here we report the effect of glycerol, glucose and acetoacetoxyethyl methacrylate (AAEM) on autoxidation and yellowing of methyl linolenate (ML_3). Progress of the reaction was followed by ^1H nuclear magnetic resonance (NMR), where the disappearance of vinylic hydrogens was measured with time, by using the methoxy protons of methyl linolenate as internal standard.

MATERIALS AND METHODS

Methyl linolenate, glucose and glycerol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification (except for glycerol). Glycerol was distilled prior to use. Acetoacetoxyethyl methacrylate was provided by Eastman Chemical Co. (Rochester, NY). The ^1H NMR spectra were obtained from a Bruker (Burlington, Ontario, Canada) 300 spectrometer at 300 MHz.



SCHEME 1

General procedure for autoxidation. To a small test tube (4 mL), equipped with a septum, glass oxygen inlet and an outlet needle, 223 μL (200 mg) of methyl linolenate was transferred under nitrogen. Oxygen was bubbled through the liquid at 45°C (heated in a water bath), at a rate of 20 mL/min, either in the dark or in the light. A definite volume of sample was taken under nitrogen every 5 hr for NMR analysis. In the case of ML_3-glycerol and ML_3-AAEM systems, 5 mol% of glycerol and AAEM were taken respectively in small test tubes, along with ML_3 and placed in the dark. For the ML_3-glucose system, ML_3 was added to a solution of glucose (5 mol% of ML_3) in methanol, nitrogen was bubbled through the solution to remove methanol before oxygen addition. The sample was then placed in the dark.

General procedure for yellowing. Methyl linolenate (34 μL, 30 mg) was spotted on the center of a white Whatman (Maidstone, England) filter paper (4.25 cm diameter). The filter paper was placed on a glass triangle in a headspace cell at 40°C (this temperature was attained by circulating heated water from a temperature-controlled water bath with a pump). A stream of air was allowed to flow through the headspace cell in the dark (by covering the headspace cell with aluminum foil) or in the light, and the absorbance of the liquid-absorbed filter paper was measured every 24 hr in a Unicam spectrophotometer equipped with a reflectance accessory. For ML_3-glycerol, ML_3-glucose and ML_3-AAEM systems, methanolic solutions containing ML_3 and 5 mol% of glycerol, glucose and AAEM were spotted separately on filter papers.

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RESULTS AND DISCUSSION

During the process of oxidation, olefinic bonds of methyl linolenate are oxidized to form initially monohydroperoxides, which undergo further reaction resulting in the loss of olefinic functionality. When the integration values of the vinylic hydrogens with respect to methoxy protons for the autoxidation of ML_3, ML_3-glycerol, ML_3-glucose and ML_3-AAEM systems in the dark and ML_3 in the light at 45°C were plotted against time, a decrease in the number of vinylic hydrogens could be observed (Fig. 1a and b). The disappearance of vinylic protons was significantly slower in the ML_3-AAEM system compared to other systems (Fig. 1a). In other words, AAEM shows a significant inhibition of autoxidation. Autoxidation of the ML_3-glucose system was slightly faster than the ML_3-glycerol and ML_3. This acceleration of autoxidation of ML_3 by glucose is similar to the observation reported for methyl linoleate by Mabrouk and Dugan (12). Glucose may enhance the autoxidation by functioning as an efficient hydrogen radical donor or by facilitating the decomposition of the monohydroperoxide, which shifts the equilibrium forward (Scheme 1). The slowing of autoxidation of methyl linolenate by glycerol is due to a delay in the rate of absorption of oxygen (13). Autoxidation of methyl linolenate in the light was faster than in the dark, particularly at the early stages (Fig. 1b).

When the yellowing studies were carried out on films of these systems at 40°C in air, all three compounds (glycerol, glucose and AAEM) showed significant inhibition at the 5 mol% level in the dark. The difference in the absorbance at 400 nm and 450 nm of the liquid-absorbed filter paper was measured as an index of yellow coloration (400–450 nm is the blue region of visible light in which yellow compounds absorb strongly) (Equation 1):

$$\text{degree of yellowing} = (A_{400} - A_{450})_t - (A_{400} - A_{450})_0 = \Delta \quad [1]$$

where $(A_{400} - A_{450})_t$ = difference in the absorbance at 400 nm and 450 nm at time t, and $(A_{400} - A_{450})_0$ = difference in the absorbance at 400 nm and 450 nm at time t = 0, which was negligible for all systems except for ML_3-AAEM (0.02).

Figure 2 shows that glycerol, glucose and AAEM exhibit significant inhibition of yellowing. The ML_3-absorbed filter paper exposed to light showed the least yellowing, probably due to bleaching of yellow compounds by light. For the ML_3-glycerol and ML_3-AAEM systems the extent of yellowing was lower, due to inhibition of autoxidation, whereas glucose showed significant inhibition of yellowing and enhancement of autoxidation. The decrease in yellowing could be due to the reduction of colored compounds or precursors of colored compounds by glucose. These observations suggest glucose to be most suitable for prevention of yellowing of indoor paint because it increases autoxidation (drying process) and inhibits yellowing of methyl linolenate. However, the useful-

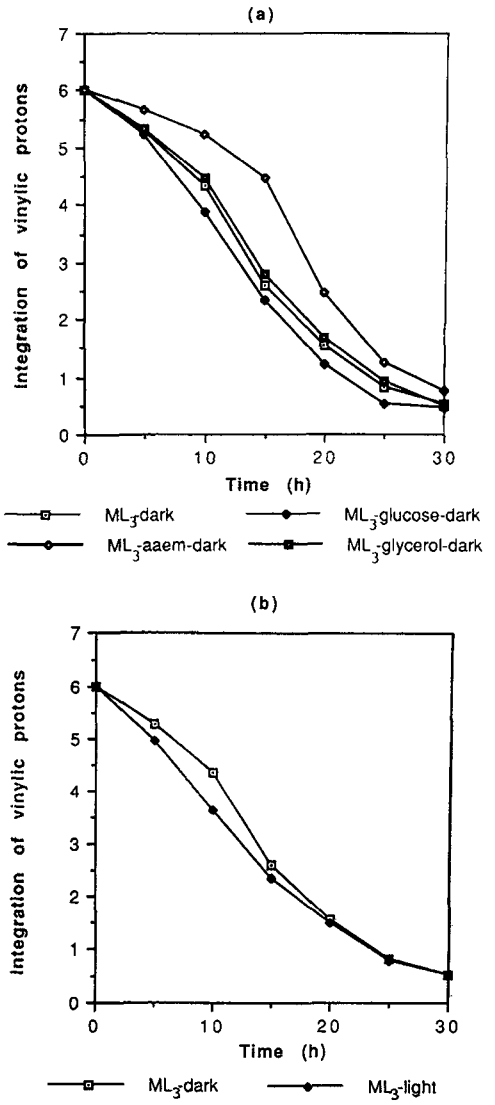

FIG. 1. a) The effect of glycerol, glucose and AAEM on autoxidation of methyl linolenate. b) Autoxidation of methyl linolenate in dark and light.

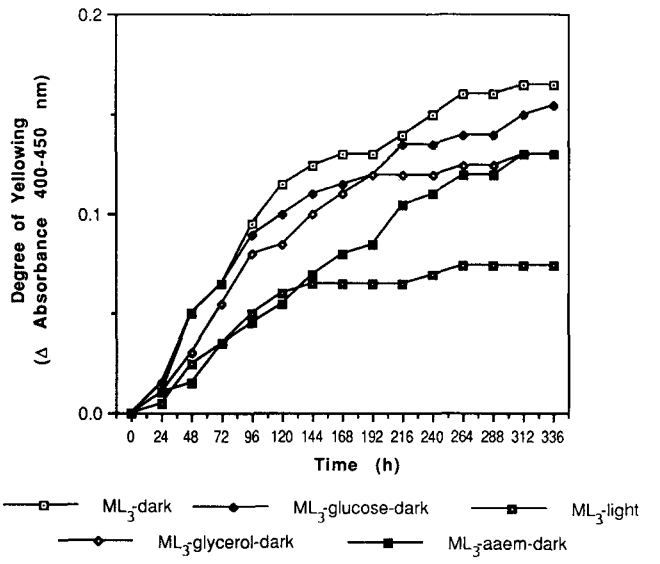

FIG. 2. The effect of glycerol, glucose and AAEM on the yellowing of methyl linolenate.

ness of glucose in inhibiting yellowing is limited, due to its poor solubility in methyl linolenate. However, this problem might be overcome by derivatizing glucose with saturated fatty acids such as stearic acid.

The mechanism by which these compounds influence autoxidation and yellowing is currently under investigation and will be reported in due course.

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