A Study of Fatty Acid Methyl Esters with Epoxy or Alkyne Functionalities

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ABSTRACT: Described are the physical and chemical properties of the methyl esters of two uncommon fatty acids: vernolic acid, containing an epoxy group, and crepenynic acid, containing a triple bond. The incorporation of an epoxy or alkyne group into the fatty acid structure is shown to greatly affect the properties compared to conventional unsaturated fatty acids. The methyl esters have been characterized and compared with ordinary fatty acid methyl esters (i.e., methyl oleate and linoleate) with respect to spectroscopic characterization [^{1}H nuclear magnetic resonance (NMR)], ^{13}C NMR, and Fourier transform infrared), rheological properties, and oxidative reactivity (using chemiluminescence). Both methyl vernoleate and methyl crepenynate could successfully be produced by transesterification under basic conditions without reaction of the epoxy or alkyne groups. Rheological measurements showed that the methyl esters had a significantly lower viscosity compared to their triglyceride analogs. Smaller differences were seen when comparing the different methyl esters where methyl vernoleate had the highest viscosity due to the presence of the more polar oxirane group. Very large differences were found with respect to the oxidation rate of the different methyl esters. Methyl crepenynate was shown to oxidize extremely rapidly, whereas methyl vernoleate was very stable toward oxidation.

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KEY WORDS: Alkyne, characterization, chemiluminescence, crepenynic acid, epoxy, methyl esters, NMR, oxidation, vernolic acid, viscosity.

Vegetable oils or triglycerides have been used for centuries to make paints and varnishes, either as themselves or as raw material for binder resins (1). Vegetable oil-based coatings can be cured either oxidatively or by other chemical cross-linking reactions. The possible curing mechanisms depend on the chemical structure of the fatty acids in the oil.

A vegetable oil consists of three fatty acids attached to a glycerol moiety *via* ester bonding (triglyceride). Numerous different fatty acids exist, and a vegetable oil typically is a mixture of many different triglyceride structures. The properties of the oil and the possible chemical reactions are, to a large extent, governed by the fatty acid pattern, structure, and fraction of specific fatty acids contained in the triglyceride structure. The fatty acid pattern not only differs between different oil crops but also depends on the growth conditions, e.g., colder climate increases the unsaturation level in linseed oil (2). Fatty acids can be obtained from the oils by ester hydrolysis or, if the methyl esters are preferred, by transesterification.

Traditionally, one of the most used vegetable oils in air-drying coatings is linseed, because of its ability to dry oxidatively under ambient conditions. Linseed oil contains large amounts of polyunsaturated fatty acids such as linoleic and linolenic fatty acids (with two and three unsaturations, respectively), and it is the amount of these unsaturations that controls whether the oil is air-drying. A triglyceride must contain on average 2.2 bis-allylic methylene groups (i.e., $\sim$CH=CH–CH_2–CH=CH$\sim$) per molecule to be considered a drying oil (3). An oil's autoxidative cross-linking must, however, be carefully controlled since the same oxidation reactions eventually will degrade the coating.

Because drying time and durability are important factors in paint formulations, different methods have been developed to improve their performance (4). The oils can be preoxidized or prepolymerized, where the latter improves not only the curing rate but also the degradation stability. The main drawback with these modifications is that they are accompanied by an increase in resin viscosity. Another way to improve the performance is to combine oils with other monomers, e.g., styrenated or maleinized oils, urethane oils, and the like (3,5).

Lately, an increasing interest has been found in the introduction of new curing mechanisms by replacement of the unsaturated sites with other functional groups. The unsaturations can easily be transformed into oxirane groups (epoxides) forming cationically curable resins (6,7). These resins have been proposed for several applications ranging from composite matrices (8) to powder coatings (2). The functionality of these resins, however, is still dependent on the level of unsaturation in the initial oil. Chemical processing is still required to achieve the functionalities desired.

Another proposed use of oils or fatty acids is as reactive diluents in coating formulations to reduce the volatile organic carbon (VOC) emissions (9). Instead of evaporating like a solvent, the reactive diluent will, apart from reducing the viscosity of the formulation, react during cure and become physically and chemically bonded in the coating. The main problem of this approach is that moieties of unreacted oil or fatty acids act as plasticizers in the film and give poor coating properties. Hence, the reactive diluent needs to be highly reactive and should not contain any inert components. Saturated fatty acids are well known to act as plasticizing agents.

The most common fatty acids are four saturated acids, i.e., lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}), and stearic (C_{18})

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acids, and three C_{18} unsaturated acids, i.e., oleic, linoleic, and linolenic acids, with one, two, and three unsaturations, respectively. Apart from these common fatty acids, there are hundreds of other different fatty acids, some with very interesting functional groups such as triple bonds, epoxy, or hydroxyl groups. Some of these fatty acids could certainly be useful for the coating technologies, but their inaccessibility is currently a major drawback. Most of these fatty acids are produced in small amounts in unusual plants, which may be difficult to harvest on a commercial scale. This obstacle may be overcome, however, by recent progress in crop development by genetically modified organism techniques. By identification of the genes responsible for producing the interesting fatty acids and transferral to new hosts, ordinary oil-producing plants, such as the flax plant, can be used. In this way traditional agricultural crops could be used to produce fine chemicals (10). Besides the advantage of being a renewable resource, specific well-defined fatty acids can be produced with fewer process steps, leading to competitive costs.

The aim of this study was to gain fundamental knowledge of the physical and chemical behaviors of the methyl esters of two unusual fatty acids, vernolic and crepenynic acids. Their rheological properties and oxidative reactivities were studied to predict their potential use in coating applications.

EXPERIMENTAL PROCEDURES

Materials. Oils extracted from the plants *Euphorbia lagascae* (containing vernolic acid) and *Crepis alpina* (containing crepenynic acid) were obtained from Svenska Lantmännen (Sweden) and were used without further purification. The fatty acid composition was determined by the supplier (Table 1). Methyl stearate (99%), methyl oleate (99%), and methyl linoleate (99%) were purchased from Sigma-Aldrich (Stockholm, Sweden) and were used as received. All other chemicals were purchased from Sigma-Aldrich or Lancaster (Lancashire, United Kingdom) and were used as received.

Characterization methods. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a 400 MHz Bruker Aspect NMR spectrometer (Karlsruhe, Germany) using $CDCl_3$ as solvent. The viscosities of the oils and fatty acid methyl esters were obtained using a Brookfield rheometer (Middleboro, MA) with a CP-40 spindle (cone and plate geometry). The viscosities were measured at temperatures from 30 to 70°C. For monitoring the oxidative stability, Tohoku chemiluminescence equipment (Tohoku Electrical Industrial Co. Ltd., Japan) was used, with a CLD-100 CL-detector and a CLC-10 CL counter. The samples were heated to 70 or 110°C with a gas flow, either air or nitrogen, of 70 mL/min. Infrared spectra were recorded on a PerkinElmer Spectrum 2000 FTIR spectrometer (Norwalk, CT) equipped with a single reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent, England). Differential scanning calorimetry (DSC) was used to determine the melting points of the methyl esters with a Mettler-Toledo DSC 820 (Columbus, OH) at a heating/cooling rate of 1°C/min. Thin-layer chromatography (TLC) was used to monitor the transesterification and to determine the fractions that contained the desired product after column chromatography. The TLC plates used (60 µm silica gel on alumina) were purchased from Merck (Schuchardt, Germany). Hexane and EtOAc were used as eluents.

TABLE 1
Fatty Acid Composition (wt%) of Oils Extracted from *Crepis alpina* and *Euphorbia lagascae*

Fatty acid	*C. alpina*	*E. lagascae*
C16:0	3.7	3.9
C18:0	1.3	1.6
C18:1	2.2	18.6
C18:2	14.3	9.2
C18:3	0.4	0.4
Crepenynic	75.9	—
Vernolic	—	65.6
C24:0	1.8	—
Other	0.4	0.7

Transesterification of C. alpina *oil. Crepis alpina* oil (4.60 g) was dissolved in 50 mL 0.02 M NaOH in methanol and refluxed for 1 h. The formed fatty acid methyl esters were extracted with 30 mL hexane. A small portion of water was added to help separate the phases. The hexane phase was dried with magnesium sulfate, and the solvent was removed on a rotary evaporator. Yield was 3.98 g methyl esters (87%).

The methyl crepenynate was purified by medium-pressure liquid chromatography (MPLC) on silica gel. The methyl ester mixture (3.98 g) was pumped onto the silica gel as a 5 wt% hexane solution and eluted with hexane and ethyl acetate, starting with pure hexane and gradually increasing to 20 vol% ethyl acetate. Yield was 0.75 g (24% of initial crepenynic acid content) pure methyl crepenynate.

^{1}H NMR ($CDCl_3$): $\delta = 0.9$ (*t*, CH_3), 1.3 (*br*, aliphatic CH_2), 1.5 (*m*, $CH_2CH_2CH_2COO$), 1.6 (*m*, CH_2CH_2COO), 2.0 (*m*, $CH{=}CHCH_2CH_2$), 2.1 (*t*, $CH_2CH_2{\equiv}C$), 2.3 (*t*, CH_2COO), 2.9 (*t*, $C{\equiv}CCH_2CH{=}CH$), 3.6 (*s*, $COOCH_3$), 5.4 (*m*, $CH{=}CH$). ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (CH_3), 17.6 ($C{\equiv}CCH_2CH{=}CH$), 19.1 ($CH_2CH_2C{\equiv}C$), 22.6 (CH_3CH_2), 25.3 (CH_2CH_2COO), 27.4 ($CH{=}CHCH_2CH_2$), 29–32 (aliphatic), 34.5 (CH_2COO), 51.8 ($COOCH_3$), 78.7 and 80.5 ($C{\equiv}C$), 125 and 132 ($CH{=}CH$), 174.7 (COO). IR: 1747 (C=O), 1654 (C=C), and 806 cm^{-1} (C≡C).

Transesterification of E. lagascae *oil. Euphorbia lagascae* oil *(*4.03 g) was dissolved in 50 mL 0.02 M NaOH in methanol and refluxed for 1 h. The fatty acid methyl esters were extracted with 2 × 20 mL hexane. A small portion of water was added to help separate the phases. The hexane phase was dried with magnesium sulfate, and the solvent was removed on a rotary evaporator. Yield was 3.48 g methyl esters (86%).

The methyl vernoleate was purified by MPLC on silica gel. The methyl ester mixture (3.48 g) was pumped onto the silica gel as a 5 wt% hexane solution and eluted with hexane and ethyl acetate, starting with pure hexane and gradually increasing to 10 vol% ethyl acetate. Yield was 1.90 g (83% of initial vernolic acid content) pure methyl vernoleate.

^{1}H NMR ($CDCl_3$): $\delta = 0.9$ (*t,* CH_3), 1.3 (*br,* aliphatic CH_2), 1.5 (*m,* CH_2CH_2CHOCH), 1.6 (*t,* CH_2CH_2COO), 2.0 (*m,* $CH{=}CHCH_2CH_2$), 2.3 (*t,* CH_2COO), 2.2–2.35 (*m,* $CHOCHCH_2CH{=}CH$), 2.9 (*m,* epoxy), 3.65 (*s,* $COOCH_3$), and 5.4–5.6 (*m,* $CH{=}CH$). ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (CH_3), 22.9 (CH_3CH_2), 25.3 (CH_2CH_2COO), 26.6 ($CHOCHCH_2CH{=}CH$), 27.8 ($CH{=}CHCH_2CH_2$–), 28.1 (–CH_2CH_2CHOCH–), 29–33 (aliphatic), 34.4 (CH_2COO), 51.8 ($COOCH_3$), 56.9 and 57.5 (epoxy), 124.3 and 132.9 ($CH{=}CH$), 174.6 (COO). IR: 1747 ($C{=}O$), 1654 ($C{=}C$), 823, and 846 cm^{-1} (epoxy).

Procedures: Chemiluminescence measurements. The gas flow was set to 70 mL/min, and the desired temperature of the oven was selected, either 70 or 110°C. When the selected temperature was reached and stabilized, 40 µL methyl ester was put into the oven and the measurement started.

Rheology. The temperature was set to 30°C, and a 0.5-mL sample was put in the sample cup. Measurements were made with different shear rates up to 1875 s^{-1}, keeping the torque in the range from 10 to 95% of maximum allowed torque. In this manner, measurements from 30 to 70°C were performed.

RESULTS AND DISCUSSION

In order to obtain any relevant data from the characterization of the fatty acid methyl esters, it is very important to have pure substances. For instance, even small amounts of impurities can significantly change the viscosity of a pure substance. Chemiluminescence measurements also will be greatly affected by the purity of the substance being examined. If a mixture of methyl oleate and methyl linoleate is to be measured by chemiluminescence, the signal from the oxidatively more reactive linoleate will completely conceal the weaker signal from the oleate.

Synthesis, purification, and spectroscopic characterization. The methyl esters were made in order to be able to study specific fatty acids. All methyl esters were synthesized by a base-catalyzed transesterification reaction. This procedure did not affect either the acetylene or the epoxy group in the crepenynic and the vernolic acids, respectively. The transesterification reaction produced a crude mixture of fatty acid methyl esters corresponding to the fatty acid composition shown in Table 1.

Methyl crepenynate and methyl vernoleate could successfully be separated from other methyl esters (mainly methyl linoleate and methyl oleate) using MPLC. A very careful selection of eluent gradients and column loading is needed, however, since methyl crepenynate and methyl linoleate are very similar in structure and have similar retention times on the column. Small changes in eluent polarity may result in poor separation. The methyl vernoleate was much easier to purify since the epoxy group introduces a larger polarity difference relative to the other oil components.

The ^{1}H NMR spectra presented in Figure 1 show a distinct methyl ester peak at 3.65 ppm and have no traces of glycerol moieties. All peaks can be assigned and correlate well with each methyl ester.

DSC. The DSC measurements showed that the melting point of methyl vernoleate is ~2°C upon heating. The melting point of methyl crepenynate is much lower, below −40°C, which was the lower limit for the DSC instrument.

Rheology. One of the most important properties of oils used in resin applications is their rheological behavior. The absolute value of the viscosity is important, for example, if methyl esters are to be used as reactive diluents in coating formulations. The viscosity will also affect other properties, such as wetting and impregnation properties.

Figure 2 presents the viscosities of the oils and the methyl esters as a function of temperature. Methyl vernoleate exhibits the highest viscosity of the methyl esters examined. This trend can be explained by the higher polarity introduced by the epoxy functionality.

The viscosity of methyl crepenynate compared with methyl stearate, oleate, and linoleate is more difficult to explain. The more extended chain due to the triple bond, i.e., a more rigid structure, is one plausible explanation for this behavior. All the methyl esters behave like Newtonian liquids within the range of shear rates measured.

Larger differences are seen when comparing the methyl esters with their corresponding oil. The viscosities are about one order of magnitude lower for the methyl esters. Again, the epoxy functional *E. lagascae* oil has a higher viscosity than the acetylenic *C. alpina* oil because of the increased secondary forces induced by the epoxy groups.

Oxidative behavior. The rate-limiting step for autoxidation of fatty acid derivatives is considered to be the abstraction of a hydrogen from the carbon backbone. This abstraction preferably occurs from a bis-allylic methylene group and continues with an addition of oxygen to the formed radical. The resulting peroxy radical can then propagate the cross-linking reaction by abstracting another hydrogen. Radicals from different chains may combine and, in this way, produce a cross-linked network (11). However, the oxidation not only produces a cross-linked network, it may also cause unwanted degradation of the formed network. For applications where oils are cured *via* other reaction mechanisms, the oxidation is mainly detrimental.

Chemiluminescence is a very sensitive method for studying early oxidation (12). This method relies on the fact that oxidation of organic materials is accompanied by photon emission. The oxidative stability can be studied by monitoring the photon emission as a function of time, temperature, and atmosphere. The uncatalyzed oxidation of methyl crepenynate and methyl vernoleate was monitored and compared with the oxidation of methyl linoleate, a fatty acid known to oxidize readily in air.

As seen in Figure 3, the methyl crepenynate oxidizes faster than the methyl linoleate, and methyl vernoleate oxidizes slower at 70°C in air. The more rapid oxidation of crepenynate, as determined by chemiluminescence measurements, indicates the presence of readily abstractable hydrogens, either the hydrogens between the unsaturations or those adjacent on the other side of the triple bond. In any event, the triple bond significantly affects the oxidation reactions compared to when only alkene groups are present, e.g., linoleate.

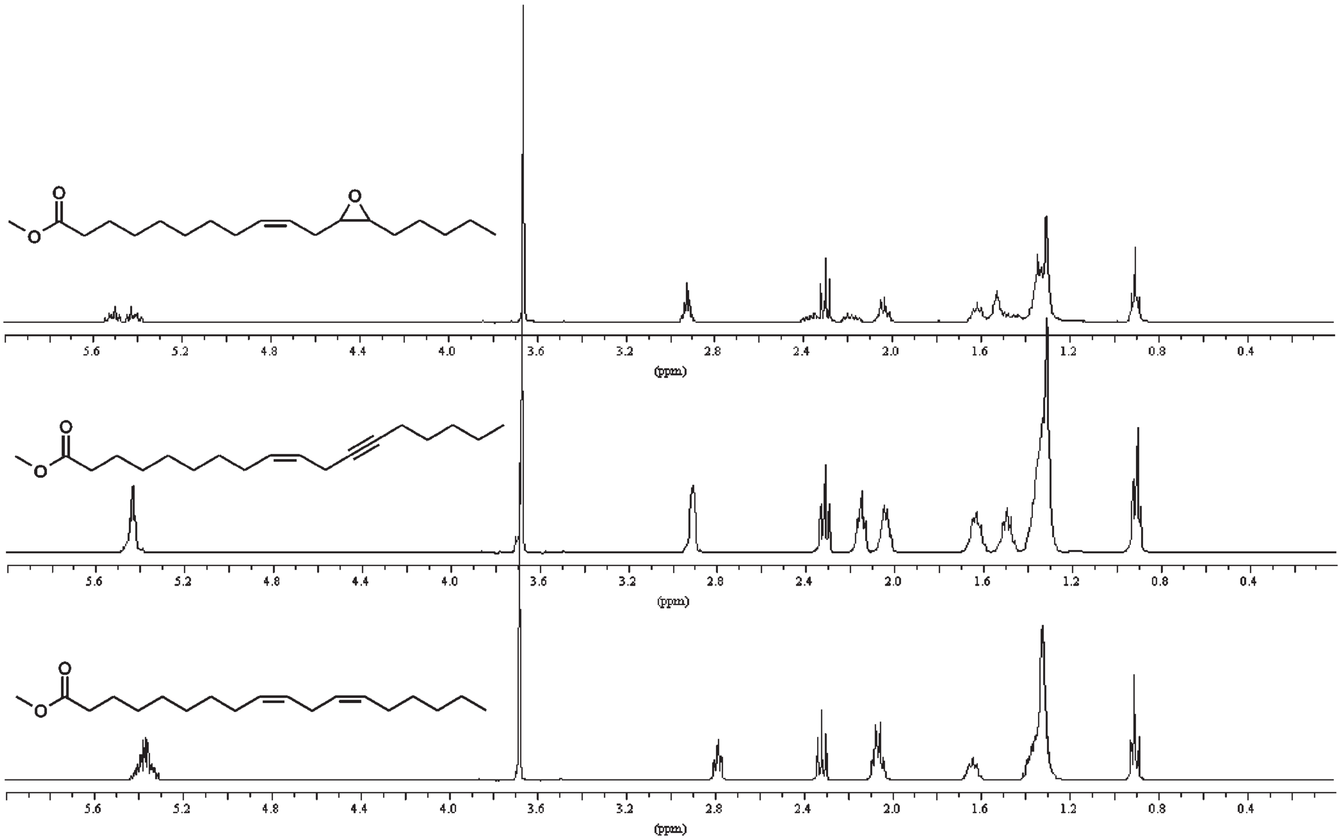

FIG. 1. ^{1}H nuclear magnetic resonance spectra and structures of methyl vernoleate (top), methyl crepenynate (middle), and methyl linoleate (bottom).

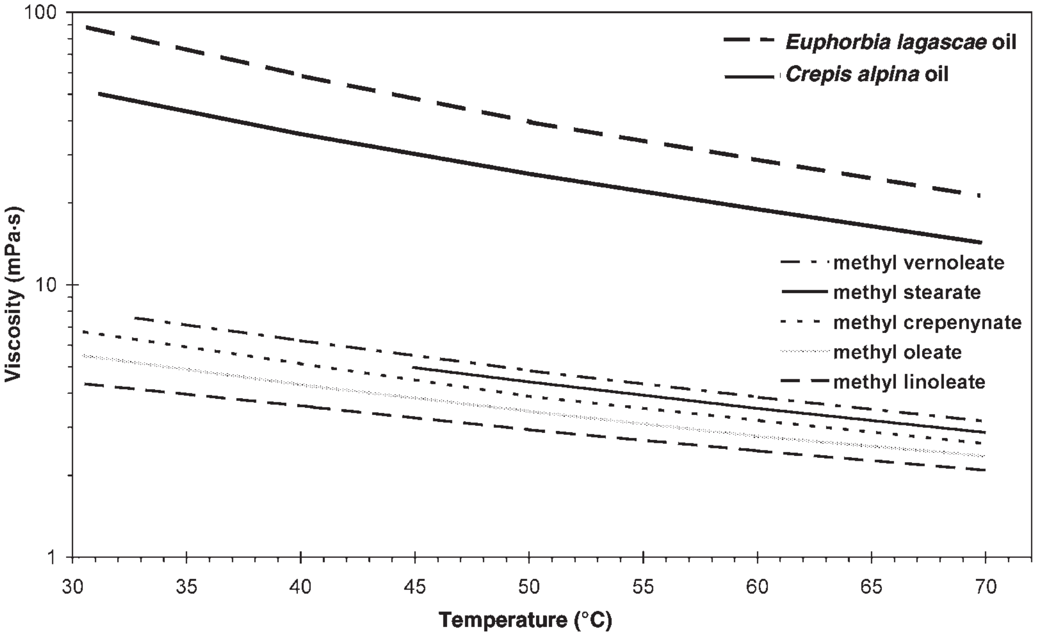

FIG. 2. Viscosities of the oils and the pure methyl esters as a function of temperature.

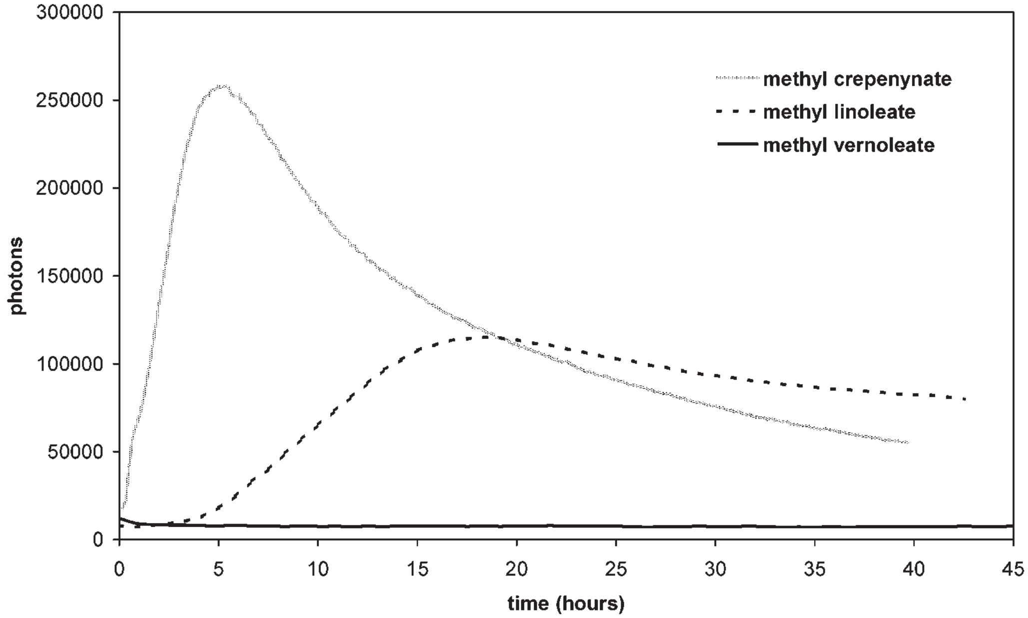

FIG. 3. Chemiluminescence trace for the methyl esters at 70°C in air.

Methyl vernoleate, on the other hand, exhibits the opposite behavior. The oxidation rate is lower compared to linoleate, indicating that the epoxy function either reduces the abstractability of the α-hydrogens or quenches the autoxidation process. Methyl vernoleate oxidizes even more slowly than methyl oleate at 110°C in air as seen in Figure 4.

Increasing the temperature from 70 to 110°C results in a significant increase in oxidation rate (Figs. 3, 4). The induction period for methyl vernoleate is decreased from more than 45 h down to 14 h, whereas the methyl crepenynate oxidizes immediately, without an induction period.

Chemiluminescence measurements were also performed under inert conditions to confirm that the signal corresponded to an oxidation reaction. The difference between an inert and an air atmosphere for methyl crepenynate can be seen in Figure 5. It is clearly seen that no appreciable reaction occurs under inert conditions.

It has been shown that methyl esters of fatty acids containing alkyne or epoxy groups can be synthesized from corresponding triglyceride oils by transesterification under basic conditions. Methyl vernoleate and methyl crepenynate exhibit low viscosities, only slightly higher than conventional methyl

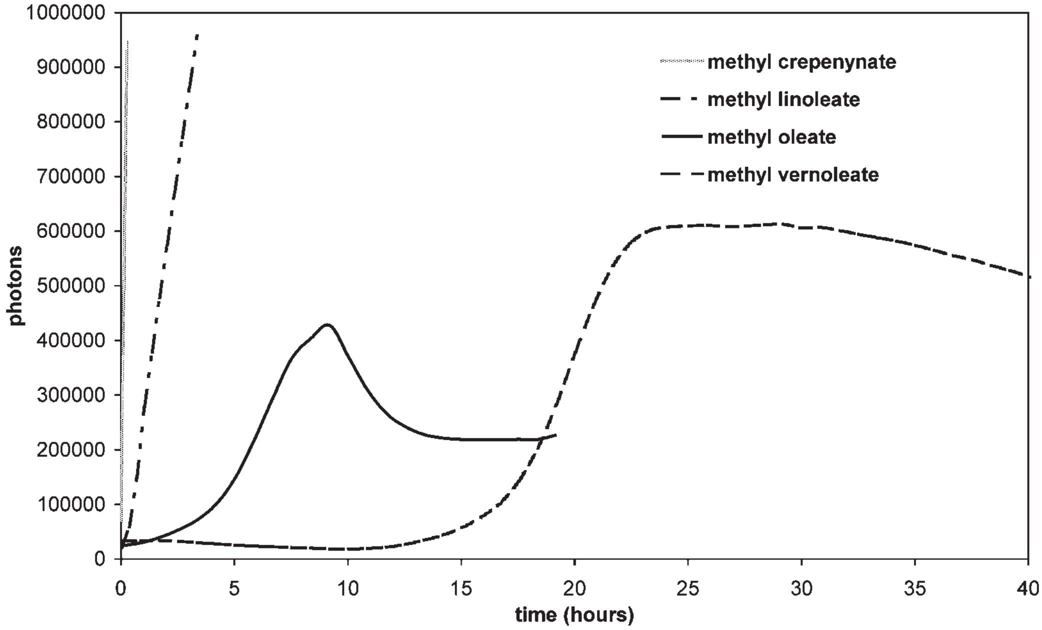

FIG. 4. Chemiluminescence trace for the methyl esters at 110°C in air.

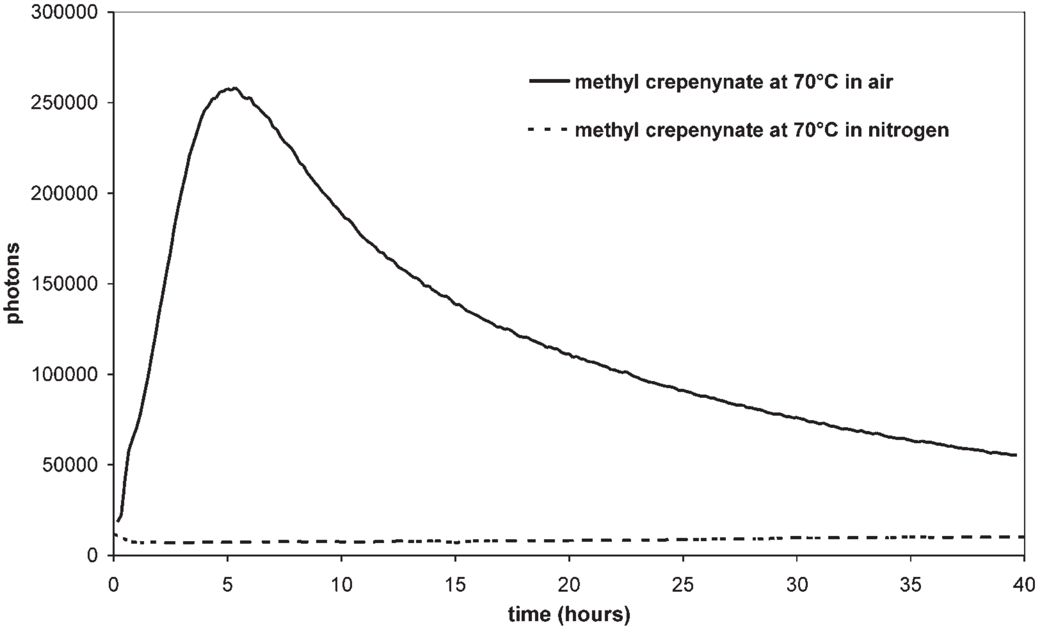

FIG. 5. Chemiluminescence trace for methyl crepenynate at 70°C in air and nitrogen, respectively.

esters such as methyl linoleate and oleate. The introduction of alkyne or epoxy groups greatly affects the oxidation rate of the methyl esters. The alkyne group increases the oxidative reactivity, while the methyl ester containing an epoxy group is remarkably stable toward oxidation.

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