Linseed Oil and Mixture with Maleic Anhydride: ^{1}H and ^{13}C NMR

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ABSTRACT: It was shown that ^{1}H NMR allowed a rapid determination of the ratio of the linolenic residues over all the others (linoleic + oleic + saturated) and ^{13}C NMR allowed a rapid determination of the ratio of linolenic over (linoleic + oleic) residues as well as the linoleic/oleic ratio in a few minutes on less than 20 mg of crude LO. After thermal treatment (220°C for 2 h, followed by cooling to room temperature), a 1:1 mixture of linseed oil (LO) and maleic anhydride (MA), which was a suspension, became limpid and remained limpid. Moreover, the viscosity of the mixture was higher than that of pure LO treated in the same way. It was shown by ^{13}C NMR and quantitative recovery of the constituents (LO and MA) through solvent separation that no reaction occurred between LO and MA during this thermal treatment. This result is in accord with DSC analysis of such a 1:1 LO/MA mixture that exhibited an exothermic effect too small (about 34 kcal/mol) to correspond to formation of a C–C bond

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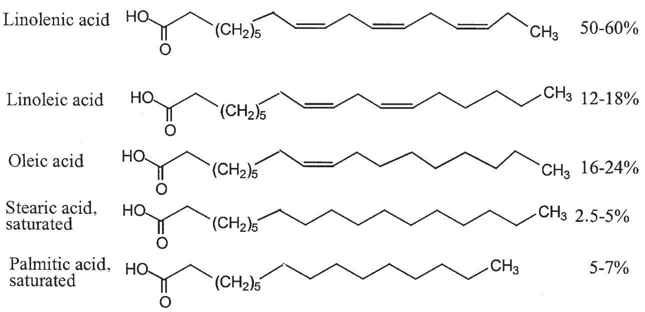
Linseed oil (LO), a complex mixture of TG (containing both unsaturated and saturated FA), is a siccative oil. The relative composition of LO (that is, the percentages of oleic, linoleic, linolenic, and saturated residues) varies slightly according to the origin of the seeds and is usually determined through conversion of the TG into methyl esters of the FA followed by analysis of the FAME (1–3) (Scheme 1).

The thermal polymerization of LO in the absence of air was studied in 1945 by Champetier (2), who pointed out the necessity of preliminary isomerization of the linolenic and linoleic nonconjugated residues into conjugated systems, thus making the Diels–Alder reaction possible. One must remember that Diels–Alder condensations are only possible between a conjugated diene (which, in LO, can be formed from isomerization of linolenic and/or linoleic residues) and a third double bond (which, in LO, can come from oleic residues or from nonisomerized linolenic and/or linoleic residues).

The necessary conditions for such isomerization are not always clear and have been claimed to be either thermal (~295°C) (2,3) or basic (4). Recently, metal-catalyzed isomerization has been clearly demonstrated (5).



SCHEME 1

Grafting of maleic anhydride (MA) onto LO isomerized in basic medium has been studied recently and Diels–Alder-type products have been proposed (4).

During work concerning grafting of MA onto LO, we studied the DSC thermograms of 1:1 LO/MA mixtures and the viscosity of such mixtures and of pure LO after identical thermal treatment. ^{1}H NMR and ^{13}C NMR of LO as well as of heated 1:1 LO/MA mixtures were also studied.

EXPERIMENTAL PROCEDURES

Samples and chemicals. The LO used came from *Linus usitatissimum* (Canada) and were a gift from Vandeputte Oil Company (Mouscron, Belgium). Determination of the composition of these LO was done through saponification/esterification and GLC analysis by the Institut du Corps Gras (Bordeaux, France) and gave: palmitic: 5–7%; stearic: 2.5–5%; oleic: 16–24%; linoleic: 12–18%; linolenic: 50–60% (the average values were: palmitic: 6%; stearic: 4%; oleic: 20%; linoleic: 15%; linolenic: 55%). Compositional variations were due to the fact that the analysis was conducted on two samples from two crops of *L. usitatissimum* seeds (Canada). MA (99%), methyl linolenate (99%), methyl linoleate (99%), and methyl oleate (99%) were purchased from Aldrich Chemicals (St. Quentin, France) and used without further purification.

Heating of LO/MA mixtures. LO (0.588 g, 0.66 mmol, 1 equiv) and MA (0.06 g, 0.66 mmol, 1 equiv) were introduced under argon into a metal tube (1 cm i.d., 5 cm length). Once hermetically closed, the tube was immersed into a salt bath reactor heated to 220°C, and this temperature was maintained for 2 h. After cooling, one aliquot of the LO/MA mixture was analyzed by NMR and a second aliquot was treated as

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follows. The mixture was dissolved in 50 mL of diethyl ether and extracted four times with distilled water (10 mL). Both phases (aqueous and organic) were evaporated under vacuum, and the residues were then characterized by ^{1}H and ^{13}C NMR. They afforded quantitatively MA (aqueous phase) and LO (organic phase). The experiment was conducted three times. Mixtures of the methyl esters of linolenic, linoleic, and oleic acids with MA were studied in a similar manner.

DSC and NMR analyses. DSC scans (in duplicate) were obtained on a Setaram DSC 131 machine (Caluire, France). A suspension of MA in LO (ratio 1:1) was introduced in a stainless steel crucible and heated to 220°C at a rate of 10°C/min under a N_2 atmosphere. Cooling to room temperature occurred at the same rate.

^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 spectrometer (Wissembourg, France). The samples (~10–20 mg) were dissolved in $CDCl_3$ (0.4–0.5 mL), and registration of the spectra were done under the usual conditions. The chemical shifts (^{1}H and ^{13}C) are given in ppm and referenced to internal tetramethylsilane.

RESULTS AND DISCUSSION

*LO (*L. usitatissimum, *Canada): NMR study.* In LO, two types of methyl signals (triplets) are expected: the linolenic type, corresponding to ethyl groups (CH_2–$C\mathbf{H}_3$) fixed on a double bond, with narrow lines located around 1.0 ± 0.05 ppm, and the linoleic-oleic-saturated type, corresponding to long saturated chains [$–CH_2–(CH_2)_n–CH_2–C\mathbf{H}_3$], with broader lines located around 0.9 ± 0.05 ppm. Specifically, the methyl triplets of oleate, linoleate, and decanoate esters are found at 0.88 ppm, whereas the methyl triplet of the linolenate ester is found at 0.97 ppm (all in $CDCl_3$).

As shown in Figure 1, the two expected types of methyl groups, either from ethyl groups of linolenic residues or from alkyl groups found in the other residues, were well separated and easily identified on the ^{1}H NMR spectrum: (i) 0.86–0.92 ppm: two methyl triplets (broad) at 0.89 and 0.90 ppm (ratio = 56:44) corresponding to the long alkyl chains of linoleic, oleic, and saturated residues (if present), and (ii) 0.95–1.01 ppm: three methyl triplets at 0.978, 0.980, and 0.988 ppm (ratio = 15:15:70) corresponding to the ethyl groups of linolenic residues.

The ratio of the linolenic residues (sum of the 0.95–1.01 ppm signals) to all the others, including the saturated residues (sum of the 0.86–0.92 ppm signals), is thus rapidly calculated to be 53:47, in good agreement with the 50–60:50–40 ratio given by the Vandeputte Oil Company as obtained by GC analysis of the ester mixture.

The ^{1}H NMR results (Fig. 1) suggest that the linolenic residues belong to three kinds of TG. Although observation of three kinds of methyl triplets on the signals of linolenic residues indicates the presence of three types of TG containing this residue, observation of two kinds of methyl triplets on the signals of the other residues (linoleic, oleic, and saturated), because they correspond to various kinds of residues, does not necessarily mean that only two kinds of TG involving these residues are present.

In the ^{13}C NMR spectrum, the different types of TG present in the oil could not be distinguished. Instead, olefinic ^{13}*C*H signals corresponding to linolenic, linoleic, and oleic

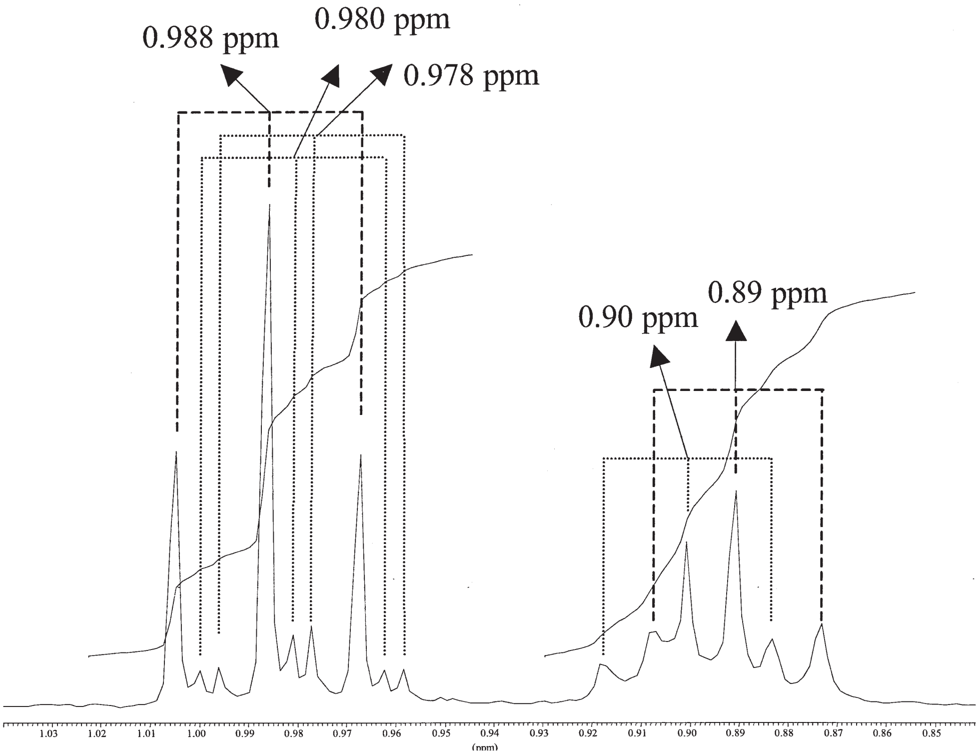

FIG. 1. Methyl signals for ^{1}H NMR (400 MHz) of linseed oil (solution in $CDCl_3$).

TABLE 1
Position in ppm (referred to TMS in $CDCl_3$) of the Double-Bond CH Singlets of Monomeric Methyl Esters, Pure LO, Pure MA, and Heated LO/MA Mixture[a]

Methyl oleate	Methyl linoleate	Methyl linolenate	LO[b] (*)/**	LO/MA[b,c] (*)/** heated	MA
				136.88/MA	136.88
130.00			130.05 (~1.7)/o	130.11 (~1.5)/o	
129.76			130.02 (~1.7)/o	130.09 (~1.5)/o	
	130.61		130.52 (~2.1)/l	130.63 (~1.7)/l	
	130.45		130.35 (~2.1)/l	130.41 (~1.7)/l	
	128.45		128.44 (~2.1)/l	128.47 (~1.7)/l	
	128.31		128.28 (~2.1)/l	128.30 (~1.7)/l	
		132.35	132.26 (~5.8)/L	132.36 (~4.3)/L	
		130.66	130.54 (~5.8)/L	130.63 (~4.3)/L	
		128.68	128.63 (~5.8)/L	128.70 (~4.3)/L	
		128.65	128.58 (~5.8)/L	128.64 (~4.3)/L	
		128.13	128.13 (~5.8)/L	128.15 (~4.3)/L	
		127.51	127.50 (~5.8)/L	127.51 (~4.3)/L	

[a] TMS, tetramethylsilane; LO, linseed oil; MA, maleic anhydride.

[b] (*) = Height of the singlets. /** = Assignment of the singlets to the various type of residues (o = oleic; l = linoleic; L = linolenic).

[c] LO/MA heated: 220°C for 2 h; analysis after cooling to room temperature.

residues were observed, and they were almost unmodified compared to the signals of the corresponding methyl esters, as seen in Table 1 (compare columns 1, 2, 3, and 4).

Although the intensities of carbon signals are only approximate, it appears that the ratio of the linolenic to (linoleic + oleic) signals is 60:40 (5.8:2.1 + 1.7), consistent with the 61:39 ratio calculated using averaged composition values [(linolenic 55%)/(linoleic 15% + oleic 20%) = 61:39].

However, the linoleic/oleic ratio (= 2.1:1.7) of 55:45 obtained by ^{13}C NMR is reversed compared to the ratio obtained from averaged values (cf. above) of the composition percentages [43:57 = 15:(15 + 20)].

LO/MA mixture: DSC, thermal treatment, NMR study. (i) DSC. DSC was used to follow the effect of temperature on the 1:1 mixture of LO and MA. The thermogram (Fig. 2) shows an endothermic effect at 55°C due to the melting of MA (which corresponds to $\Delta H° = 153$ J/g of MA) and an exothermic effect starting at 185°C ($\Delta H° = -145$ J/g), which could reasonably be due to formation of a "stable mixture" between LO and MA but not to a reaction with the formation of a covalent bond. Indeed, if one takes 970 g as the average mass of 1 mol of a 1:1 LO/MA mixture (calculated from averaged values of LO composition given above), the 145 J/g value corresponds to ~141 kJ/mol (about 34 kcal/mol) and therefore does not correspond to formation of a C–C bond [83–85 kcal/mol (6)].

It is worth noting that when the sample was cooled to room temperature, no exothermic peak, which would correspond to the crystallization of MA, was observed.

(ii) Thermal treatment. A suspension of MA in LO (LO/MA ratio = 1:1) was heated to 220°C for 2 h in the absence of air (cf. Experimental Procedures section). After returning to room temperature, the sample (called heated-LO/MA) was more viscous (14,000 cP) than the starting LO heated under the same conditions (50 cP) but was and remained limpid, indicating that MA did not crystallize out upon cooling.

When the same experiments were conducted on suspensions of MA in methyl linoleate, methyl linolenate, and/or methyl oleate, MA crystallized out in all cases after cooling to room temperature.

(iii) NMR. The ^{13}C NMR study of heated-LO/MA (220°C, 2 h) mixtures was done by dissolving about 10–20 mg of the mixture (after cooling) in $CDCl_3$ (all material soluble). It appeared (Table 1) that all the CH singlets observed in the starting LO were still present and at the same position (within experimental variations) together with the CH singlet of MA (compare columns 4, 5, and 6 of Table 1). No double-bond CH signals and no saturated CH signals, which could correspond to substituted cyclohexenes formed from Diels–Alder reac-

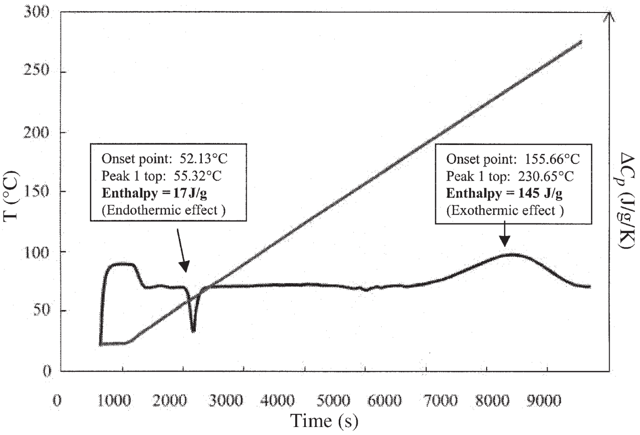

FIG. 2. Heat exchange upon heating a 1:1 mixture of linseed oil and maleic anhydride. Values for enthalpies are reported as per gram of mixture. Temperatures are read on the temperature gradient line at the crossing with a vertical line drawn up from the minimum and from the maximum. C_p, heat capacity at constant pressure.

tions, were observed. The ^{1}H NMR spectrum also exhibited no change between the starting pure LO and the heated-LO/MA mixture (no change in the saturated/unsaturated proton ratio).

Thus, it can be concluded that no covalent bond was formed between LO and MA during heating, as a covalent bond would not be disrupted upon dissolution in $CDCl_3$. This was also confirmed through full recovery of pure LO and MA after water extraction of a diluted diethyl ether solution of the heated-LO/MA mixture. Thus, although the viscosity of a 1:1 LO/MA mixture increased after thermal treatment and although the mixture remained limpid after this treatment, it was shown by NMR that no reaction occurred between LO and MA. This was confirmed by quantitative recovery of both constituents through solvent extraction. This conclusion is in accord with the DSC analysis, which showed that the observed exothermic effect could not correspond to formation of a C-C bond.

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