Polymerization of Safflower and Rapeseed Oils

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ABSTRACT

Rates of polymerization of oils from 2 safflower and 2 rapeseed varieties were measured in the air and under vacuum. Thermal polymerization rates showed a stronger dependence on the degree of unsaturation than on oxidative polymerization. Molecular weight distributions of polymerized oils were determined by size exclusion chromatography, and the relationship between viscosity and weight-average molecular weight was determined.

INTRODUCTION

Traditionally, vegetable oils have been used not only for edible purposes, but for such nonfood applications as drying oils in paint, soaps, cosmetics, pharmaceuticals, synthetic rubber, and emulsifiers. Recently, oilseed crops have also been considered as a liquid fuel source, and vegetable oils have shown potential as a direct substitute for diesel fuel. However, vegetable oils are inherently less stable than commercial diesel fuels because of the high degree of unsaturation of vegetable oils and the consequent susceptibility to polymerization or gum formation.

Nearly all previous work on gum formation and deterioration of vegetable oils has been concerned with the drying oils used in paints, varnishes, and other coatings. For these applications, highly unsaturated oils such as linseed, safflower and soybean have been used. The mechanisms for gum formation by oxidative and thermal polymerization in drying oils have been summarized in several reviews (1-3). Oxidative polymerization occurs by the interaction of double bonds and oxygen to form peroxides. Conjugation of double bonds occurs to stabilize hydroperoxides. A free-radical chain reaction is initiated as hydroperoxides decompose and the subsequent chain-growth polymerization reaction gives high molecular weight, crosslinked products. Although rates of oxidative polymerization increase with the extent of conjugation and unsaturation, quantitative relationships have not been established. The rates of oxidation of films of triolein, (18:1), trilinolein (18:2), and trilinolenin (18:3) have been shown to be 1:20:330 (4). Relative rates of oxidation of methyl oleate, methyl linoleate and methyl linolenate were determined to be either in the order 1:12:25 or 1:2:4 (3,5). Decomposition of oxidized methyl esters of triglycerides and fatty acids has shown that oligomers as large as tetramers are formed as would be expected in a chain-growth polymerization reaction (6).

Thermal polymerization occurs in a step-growth polymerization in a Diels-Alder reaction (1) or a free-radical mechanism (7), but both mechanisms show the same trend with vegetable oil composition (8). Thermal polymerization is favored by the presence of conjugated double bonds and, consequently, thermal polymerization, and the rate-determining step appears to be the isomerization of nonconjugated to conjugated forms.

For most free-radical polymerizations, such as oxidative polymerization, activation energies for propagation are close to 5 kcal/mol and overall activation energies are 15-20 kcal/mol (7). Activation energies for thermal polymerizations are ca. twice that of free-radical, chain-growth polymerizations are ca. twice that of free-radical, chain-growth polymerications (9,10), and thermal polymerization is negligible at temperatures below 250 C.

The aim of this study was to determine rates of thermal and oxidative polymerization of vegetable oils as functions of oil composition and temperature. Also, polymerization products were characterized by size exclusion chromatogrraphy as a measure of polymerization rates and as a guide for identifying the polymerization mechanism.

EXPERIMENTAL PROCEDURES

Safflower seeds were obtained from California Fats and Oils, Inc., Richmond, CA and rapeseed was grown in northern Idaho and obtained locally. Seeds were extracted on an expeller press (CeCoCo Type 52). This expeller press was operated with an oil-recovery efficiency of ca. 75%. The extracted oil was allowed to settle in 50 gal drums and filtered through a 3-stage filtering system consisting of a recleanable Gresen Hydraulics prefilter, a Napa 1515 20 μm oil filter and a caterpillar IP2299 4-5 μm fuel filter.

Kinematic viscosity was measured with Cannon-Fenske viscometers in a water bath at 37.8 C (100 F). Fatty acid composition was determined by the conversion of oils to methyl esters (11) and the separation of esters in a 6-ft, 1/8. O.D. stainless-steel column packed with 10% Silar 10 C on 100/120 GAS CHROM Q at 180 C in a Varian 1400 gas chromatograph.

Size exclusion chromatographs were obtained on a Beckman Model 332 high performance liquid chromatograph (HPLC) with a Model 155-00 UV-Visible variable wavelength detector and a DuPont 60 Angstrom size exclusion column. UV spectroscopic grade hexane was used as HPLC solvent, and benzene was added to each sample as an internal standard. The flow rate was 1 mL/min. Chromatograms were recorded on a Hewlett Packard 3390 A recording integrator.

Thermal polymerization samples were sealed under vacuum in glass ampoules and heated in an electric furnace. Oxidative polymerization samples were heated in open glass beakers in a forced-air convection oven.

RESULTS AND DISCUSSION

Vegetable oils with a wide range of unsaturation were selected (Table I). The high linoleic acid safflower and the high oleic acid safflower variety represent the 2 extreme of unsaturation among the common vegetable oils, resulting from the alteration of a single gene. A comparison of these 2 safflower varieties demonstrates the effects of unsaturation with little interference from other vegetable oil properties.

Bulk viscosities of vegetable oils were used as a measure of the degree of polymerization. Relative viscosity measurements for oxidative polymerization at 260 C are shown in Figure 1. Viscosity data was fitted to an exponential model,

$$\nu = ae^{bt} \qquad [1]$$

where ν represents kinematic viscosity, t is time, and a and b are constants determined by the data fitting (Table II).

Rates of oxidative and thermal polymerization were measured at 240-300 C for linoleic and oleic safflower and high erucic rapessed (12). Thermal polymerization was negligible below 240 C. At 240 C, the viscosity of high linoleic safflower oil increased by a factor of 32 over 11 hr in an air environment and shows no change in a nitrogen environment. High erucic acid rapeseed showed a viscosity increase ca. 1/4 that of linoleic safflower for oxidative polymerization at 240 C.

TABLE I

Composition of Vegetable Oils

	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Eicosenoic 20:1	Linolenic 18:3	Erucic 22:1
	Percentage by weight methyl esters						
Linoleic safflower	5.87	1.53	8.84	83.76	–	–	–
Oleic safflower	4.75	1.39	74.12	19.74	–	–	–
Rapeseed (sipal variety)	4.29	1.26	59.89	21.12	–	13.19	–
Rapeseed (Dwarf Essex variety)	2.97	0.80	13.09	14.09	7.41	9.71	50.72

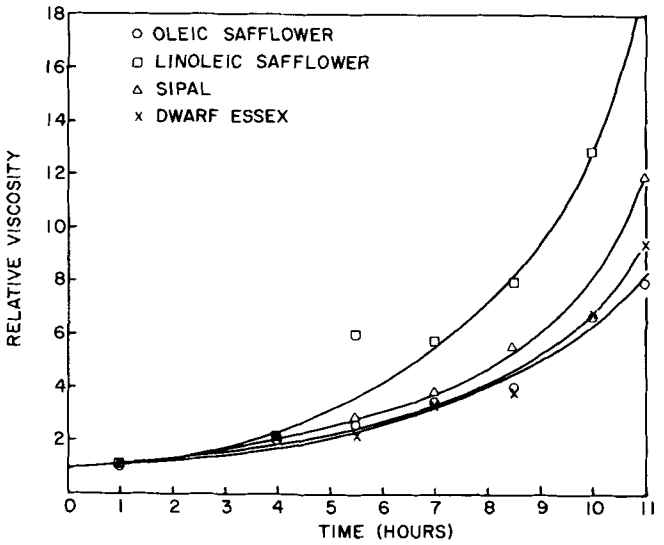

FIG. 1. Relative viscosities of oxidized vegetable oils vs polymerization time at 260 C.

TABLE II

Viscosity Constants for Oxidative Polymerization

Oil type	a (mm^2/s)	b (h^{-1})	Temperature (C)
Linoleic safflower	27.5	0.28	260
Sipal rapeseed	32.7	0.21	260
Dwarf Essex rapeseed	44.3	0.19	260
Dwarf Essex rapeseed	43.0	0.16	240
Oleic safflower	36.4	0.19	260

Rates of thermal polymerization showed a stronger dependence on the degree of unsaturation than oxidative polymerization. Relative rates of oxidative polymerization of oleic and linoleic safflower were ca. 1:3 at 260 C. Relative rates of thermal polymerization of the same 2 oils were ca. 1:30 at 320 C. Relative viscosities of the 4 vegetable oils for thermal polymerization at 320 C are shown in Figure 2. The trend of thermal polymerization rates of the 4 oils was the same as with oxidative polymerization have similar dependencies on unsaturation. The strong temperature dependency of thermal polymerization rates is apparent from data for thermal polymerization of linoleic acid fitted to equation 1 (Table III).

The relationship between viscosity and molecular weight was determined by size exclusion chromatography for thermal polymerizations. A typical chromatogram is shown in Figure 3. Benzene was used as an internal standard and had a retention time of ca. 10.5 min. Eight distinct peaks

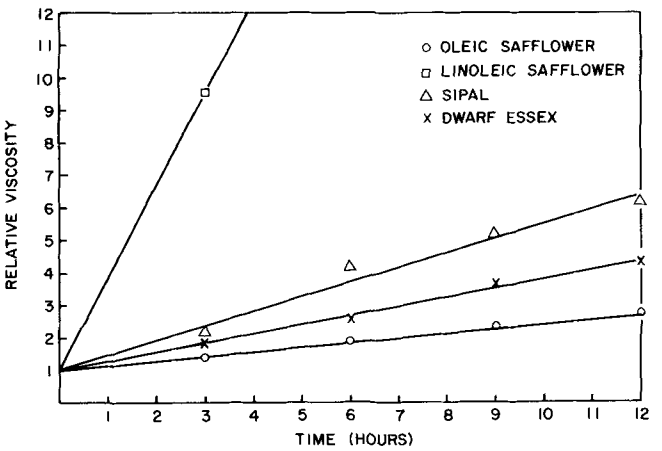

FIG. 2. Relative viscosities of thermally polymerized vegetable oils at 320 C.

TABLE III

Viscosity Constants for Thermal Polymerization of Linoleic Sfflower

Temperature (C)	a (mm^2/s)	b (h^{-1})
280	36.8	0.10
300	65.4	0.21
320	33.3	0.67

were observed in the chromatogram shown in Figure 3 corresponding to the triglyceride monomer with a retention time of 8.3 min through the octamer with a retention time of 5.6 min. Oligomer retention times were used to provide calibration curves up to a molecular weight of ca. 11,000 (Fig. 4). All 4 oils gave similar calibration curves. These calibration curves were linear over a molecular weight range of 2,500 to 11,000 and were extrapolated to higher molecular weights to estimate molecular weights at higher retention times.

Ultraviolet (UV) rather than refractive index detection was used for thermal polymerization as UV detection sensitivity was much greater. However, the UV molar extinction coefficient varies with molecular structure and increases with increasing conjugation. If the assumption is made that the response of the UV detector was proportional to the concentration of repeating units being eluded at any given relative retention time, the chromatograms represented molecular weight distribution curves for the thermally polymerized oils. Chromatograms indicated that molecular weight distributions were complex. Oligomers with chain lengths of 4-8 units were observed at low extents of reaction indicating a chain-growth, free-radical polymerization.

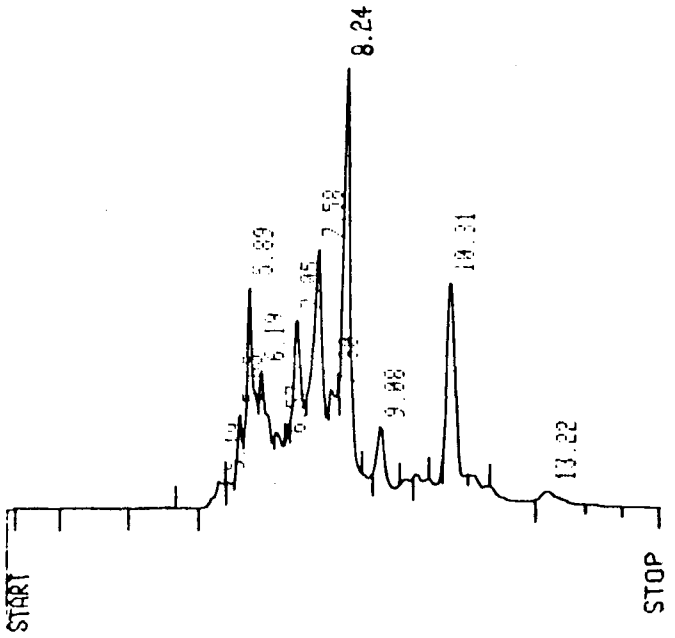

FIG. 3. Chromatogram of Dwarf Essex heated under vacuum at 320 C for hr. Analyzed by size exclusion chromatography with UV detection at 206 nm, flow rate 1 mL/min.

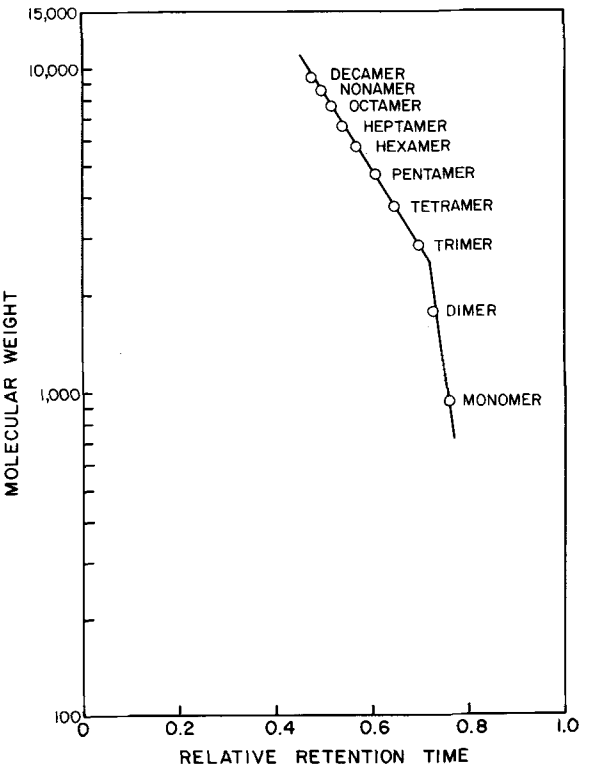

FIG. 4. Calibration curve of log of weight-average molecular weight vs relative retention time for Dwarf Essex.

In Figure 3, the concentrations of hexamer and heptamer were 10.4% and 18.9% when the triglyceride monomer concentration was 32.2%. The weight fractions of oligomers were determined by integrating the corresponding chromatogram peaks to determine peak area percentage. By multiplying the area percentages by their corresponding molecular weights and summing, the weight-average molecular weights were determined.

A plot of measured bulk viscosities for thermal polymerization at 320 C vs weight average molecule weights determined by size exclusion chromatography is shown in Figure 5. These data were fitted by the relationship

$$\nu = 1.39 \times 10^{-4}\ \bar{M}_W^{1.65}\ (mm^2/s) \qquad [2]$$

where $\bar{M}_W$ is the weight-average molecular weight. This relationship is of the same form as the relationships describing polymer melt viscosities (13). Linoleic safflower was not included in this correlation. The high degree of linoleic safflower unsaturation and the rapid thermal polymerization accompanied by the extensive crosslinking of linoleic safflower produced viscosities higher by a factor of ca. 2 than predicted by Figure 5 and equation 2.

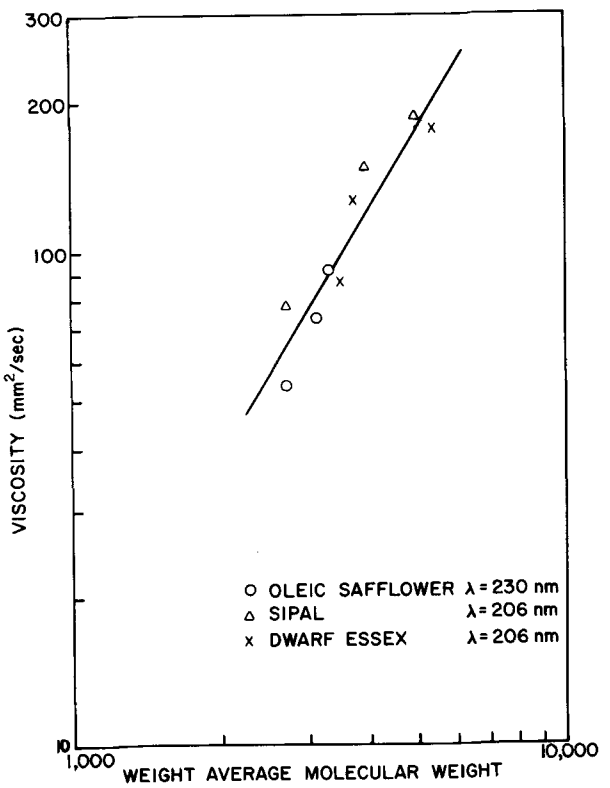

FIG. 5. Logarithmic plot of viscosity vs weight-average molecular weight of thermally polymerized vegetable oils.

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Evening Primrose (*Oenothera* Spp.) Oil and Seed

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ABSTRACT

Evening primrose (*Oenothera* spp.) seed contains ca. 15% protein, 24% oil, and 43% cellulose plus lignin. The protein is unusually rich in sulphur-containing amino acids and in tryptophan. The component fatty acids of the oil are 65–80% linoleic and 7–14% of γ-linolenic, but no α-linolenic acid.

The 1.5–2% unsaponifiable matter has a composition very similar to that of cottonseed oil. The sterol fraction contains 90% β-sitosterol and the 4-methyl sterol fraction contains 48% citrostadienol; γ-tocopherol dominates its class, with some α- but no other tocopherols.

INTRODUCTION

Evening primrose (*Oenothera* spp., particularly *Oenothera biennis*) is of special interest because its seed contains an oil characterized by its content of γ-linolenic acid (all *cis*-6:9:12-octadecatrienoic acid) (1), sometimes also designated 18:3-ω6. Although comparatively scarce in seed oils, this acid also occurs in a number of other oilseed bearing plants such as the *boraginaceae* (2) and *aceraceae* (3) families. In these oilseeds, however, it is normally accompanied by the common α-linolenic acid. γ-Linolenic acid also occurs in unicellular organisms such as the blue-green alga *Spirulina* (4), fungi such as the phycomycetes (5) and protozoa, e.g., *tetrahymena pyriformis* (6). Particular interest attaches to the recent observation that γ-linolenic acid is present in human milk fat (7). Indeed, this acid is probably more widely distributed than is at present realized since simple methods have only recently become generally available for identifying and differentiating it from α-linolenic acid.

At present, evening primrose oil is the most important source of γ-linolenic acid, which is in growing demand for its clinical and pharmaceutical applications as a very active essential fatty acid, and the precursor of prostaglandin E_1 and its derivatives (8). Studies in this field are very active, e.g., at the laboratories of Efamol Research Inc., Kentville, Nova Scotia, Canada. Although the evening primrose plant does not produce a high yield of seeds compared with the well-known commercial oilseeds, it is preferred to other sources of γ-linolenic acid because it is easy to produce and because it does not contain any α-linolenic acid. Very little information on this seed or its oil composition has been published. The object of this communication is to report some compositional characteristics and properties of evening primrose oil and seed in order to assist in setting quality standards and to provide means for authentication.

EXPERIMENTAL PROCEDURES

Materials

Evening primrose seed and oil samples were supplied by Efamol Ltd., Efamol House, Woodbridge Meadows, Guildford, Surrey GU1 1BA, England. The extensive seed production and plant breeding programs in progress under the auspices of this company have made a wide range of seed types available. Cottonseed oil (unrefined) was from Tropical Products Institute, 52–62 Grays Inn Road, London WCIX 8LU, England.

Seed analyses were by standard methods (9), except for fiber analysis, which was carried out by the acid-detergent method of the USDA (10). Component fatty acids were determined by gas-liquid chromatography (GLC) of methyl esters prepared by transmethylation of the oil with sodium methoxide in methanol. A 10% EGSSY (ethylene glycol succinate-methyl silicone copolymer, U.S.P. 3,253,401) column operating at 180 C was used. Injection point and flame ionization detector were at 200 C in the Pye 104 Gas Chromatograph with a nitrogen flow rate of 30 mL/min.

Saponification of the oil was carred out by reflux for 1 hr of 10 g of oil, 10 mL 60% KOH solution, 60 mL ethanol and 10 mL light petroleum (b.p. 60–80 C). After cooling, 100 mL of distilled H_2O was added and unsaponifiable matter (USM) extracted from the mixed soaps by three successive extractions with diethyl ether (100 mL each). After washing with water and drying over anhydrous Na_2SO_4, the combined extracts were evaporated to dryness to recover USM.

The USM sample (30 mg) was applied (in benzene) to the baseline of a silica gel G60 plate for preparative TLC. The chromatogram was developed with hexane/diethyl ether (4:1), and the plate dried and sprayed with a 0.01% of Rhodamine 6G in ethanol. Observed under UV, the separated fractions, in decreasing order of polarity, showed orange, faint orange-yellow, orange-yellow and two or three dull purple fluorescent bands corresponding to sterols, 4-methyl sterols, triterpene alcohols and two or three tocopherols, respectively. The bands were scraped from the plate and organic material quantitatively extracted with diethyl ether and weighed.

Sterols and 4-methyl sterols were analyzed directly by GLC in a Pye 104 Chromatograph, using a 3% SE-30 column operating at 250 C with a nitrogen flow rate of 50 mL/min. Triterpene alcohols could be handled under the same conditions but slightly better resolution was obtained by derivatizing them as acetates (11), which were run on a 1% SE-30 column operating at 230 C and flow rate of 50 mL/min.

Tocopherols were separated from USM by the same method used for the other classes of components, α-, γ- and δ-tocopherols appearing as separate bands, which were individually identified by comparison with standards. For quantitation, samples were spiked with known levels of stigmasterol and run on a 3% SE-30 column operating at 240 C with a flow rate of 50 mL/min.