

Pyrolysis Studies with Jojoba Oil

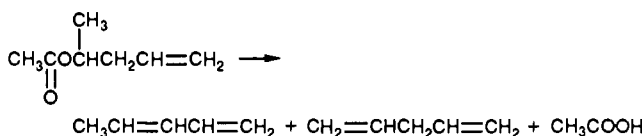
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Jojoba oil, a mixture primarily of eicosenyl eicosenoate and docosenyl docosenoate, was pyrolyzed via intramolecular elimination to produce dienes and fatty acids in the C₁₈-C₂₄ range. Temperatures of 350-400 °C and reduced pressure are required to exclude thermal cracking to low molecular weight olefins.

INTRODUCTION

Despite the considerable amount of work reported on the pyrolysis of esters (Depuy and King, 1960) since the first recorded example in 1854 (Heintz, 1854), there have been few recorded examples of the pyrolysis of monocarboxylic acid esters in which a double bond is present in either the alcohol or the acid portion of the molecule. Maccoll [private communication, see Depuy and King (1960)] has reported a mixture of 64% 1,3- and 30% 1,4-pentadiene from the pyrolysis of 4-acetoxy-1-pentene.



In this special case, as expected, the conjugated diene predominated over the unconjugated isomer despite the availability of more β hydrogen atoms on the adjacent carbon atom.

Jojoba oil is a mixture of esters—predominantly eicosenyl eicosenoate, docosenyl docosenoate, eicosenyl docosenoate, and docosenyl eicosenoate (Miwa, 1971; Miwa et al., 1979; Spencer et al., 1977). Small amounts of C₃₆, C₃₈, C₄₆, and C₄₈ unsaturated analogues are also present.

Thus, jojoba oil represents a readily available source of esters with a double bond in both the alcohol and acid portions of the molecule. Controlled pyrolysis should follow the concerted elimination path common to the pyrolysis of saturated esters and should generate a mixture of unsaturated acids and diolefin. The only previous paper on the pyrolysis of jojoba oil involved cracking of the oil over a zeolite catalyst at 500 °C to produce CO₂ and low molecular weight olefins (Weiss et al., 1979). Others (Schwab et al., 1988) have reported pyrolysis data on several triglyceride oils using a destructive distillation technique to produce low molecular weight hydrocarbons useful as diesel fuel [see Schwab et al. (1988) for numerous other papers on related cracking studies].

MATERIALS AND METHODS

Materials. Jojoba oil was obtained from JMC Technologies, Inc. (Phoenix, AZ). It was analyzed by mass spectroscopy and by GLC and established as a mixture of esters of monounsaturated acids and monounsaturated alcohols [see Miwa et al. (1975)]. Analysis showed 0.6% C₃₄, 3.5% C₃₆, 24.9% C₄₀, 58.0% C₄₂, 11% C₄₄, 1.7% C₄₆, and 0.3% C₄₈. The acid number was 0.2. The product was washed with dilute aqueous ferrous ammonium sulfate to remove any peroxides, dried over anhydrous Na₂SO₄, filtered, and stored under nitrogen.

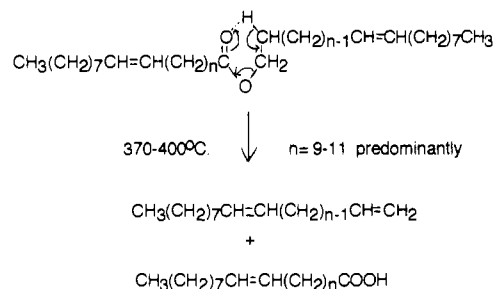


Figure 1. Concerted elimination mechanism for jojoba pyrolysis.

Table I. Analysis of Diolefin Fraction

	GLC analysis
hexadecadiene, %	1.2
octadecadiene, %	5.1
eicosadiene, %	60.0
docosadiene, %	30.7
tetracosadiene, %	3.0

Table II. Mass Spectrometer Analysis

	mass no.		other fragments
	theor	found	
hexadecadiene	222.3	223	205, 149, 111, 97, 83, 69
octadecadiene	250.4	252	149, 138, 96, 82, 65, 55
eicosadiene	278.5	278	220, 138, 96, 82, 64, 55
docosadiene	306.6	306	180, 152, 110, 96, 82, 64, 55
tetracosadiene	334.6	335	180, 152, 124, 96, 82, 64, 55

Pyrolysis of Jojoba Oil. A 100-g sample of jojoba oil was heated under a stream of nitrogen in a 500-mL flask fitted with a thermometer, a Vigreux column and an air condenser to which were attached a dry ice trap and a Ba(OH)₂ tube to absorb any carbon dioxide. Vacuum of 200 mm was applied to prevent excessive secondary cracking. The temperature of the oil was raised at 10 °C/min to 370 °C, at which time pyrolysate was observed in the condensing system. The temperature was maintained at 370-410 °C, and high boiling liquid distilled at a rate of about 2 mL/min. After 5 h, the reaction was terminated and 90 g of pyrolysate was obtained. Distillation gave 84 g of liquid boiling at 190-320 °C at atmospheric pressure. The entire distillate was dissolved in 200 mL of hexane and eluted through activated alumina to give 41 g of eluate which was analyzed by GLC and GC/MS. The adsorbed phase on alumina was desorbed using first a 1:1 mixture of ether and finally hot ethanol. Evaporation of the solvent gave 35.5 g of acids, which were separated and identified by GLC, GC/MS, and infrared spectroscopy. Less than 0.001 mol % of BaCO₃ was obtained, indicating that decarboxylation was not a factor in the pyrolysis. At these temperatures jojoba oil has a negligible vapor pressure, and no unreacted jojoba oil was observed in the distillate.

Analyses. Infrared spectra were used to establish structures of mixed acid, and a Perkin-Elmer Model 720B instrument was

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Table III. Analysis of Acid Fraction

acid	GC area, %	MS parent peak
hexadecanoic	0.1	256
hexadecenoic	1.2	254
octadecanoic	0.2	284
octadecenoic	7.3	282
eicosenoic	58.3	310
docosenoic	30.1	338
tetracosenoic	2.8	366

used for these analyses. Gas chromatographic data and mass spectral data were obtained on a Hewlett-Packard 5995 GC/MS unit.

RESULTS AND DISCUSSION

The pyrolysis of esters is a simple reaction, the yields of products are excellent, and the separation of product mixtures is relatively easy. The pyrolysis is generally first order in kinetics and proceeds by a cis elimination (Depuy and King, 1960; Bordwell and Landis, 1958), thus supporting a cyclic transition state as shown in Figure 1.

Pyrolysis of jojoba oil at 350–400 °C under 100–200-mm vacuum gave a mixture of diolefins and unsaturated acids. Traces of monoolefins were also detected. The acids were separated from the diolefins on alumina; hexane eluent was used to remove the diolefins, and acid was recovered using hot ethanol.

Analysis by GLC of the diolefin fraction (48 wt % of the total distillate) showed the presence of major amounts of eicosadiene and docosadiene along with lesser quantities of hexadecadiene, octadecadiene, and tetradecadiene. Results are given in Table I.

Mass spectra data, provided in Table II, establish the mass numbers for the five diene components. In all cases, the parent peaks matched the theoretical mass numbers.

The individual components in the acidic fraction (42 wt % of the total pyrolysate) were identified by infrared and GC/MS. Results are given in Table III.

The presence of isomeric structures in the various dienes was demonstrated by GC/MS analysis of an expanded

Table IV. Expanded Eicosadiene Peak

m/e	retention time, min	area, %
278	13.94	2.8
278	14.06	11.2
278	14.16	83.9
278	14.21	2.1

eicosadiene peak (see Table IV). That expansion showed four eicosadiene peaks, all of parent mass number 278. The isomers are believed to have resulted from double-bond shifts rather than chain branching. More detailed separation and analytical data on all of the dienes and acids will be reported in a separate publication.

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