Secondary Products from High Pressure Hydrogenation of Crambe Oil[1]

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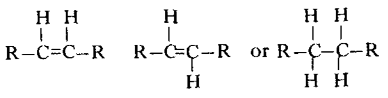
ABSTRACT

Hydrogenation of crambe oil, mainly an α,α'-dierucoyl triglyceride, in the presence of cadmium promoted copper-chromite provides long chain waxes being sought as sperm whale oil replacements. Gas liquid chromatography and gas chromatography-mass spectrometry analyses of secondary products indicate, however, that reduction proceeds rather differently from Adkins-type hydrogenations of triglycerides over copper-chromium oxide catalysts. Mono- and diunsaturated alkenes ranging from C_{16}-C_{24}, odd chain lengths included, constitute ca. 1% of the product. Esters of crambe acids with methyl, ethyl, n-propyl, and isopropyl alcohols account for less than 5%. These alcohols and traces of 1,2-propanediol from the hydrogenolysis of glycerol occur in either the head gas or the reaction mixture or both. In contrast to published results for Adkins-type hydrogenations of triglycerides, n-propyl alcohol is far more abundant than isopropyl alcohol or 1,2-propanediol. Isopropyl esters of C-18 acids are not present, and those of C-22 acids constitute no more than 2% of the total esters. Low proportion of isopropyl esters and enrichment of C-22 acids in the secondary products compared with C-18 acids suggest that the acyl substituent at the β-position of glycerol is eliminated during hydrogenation of crambe oil with a Cd-Cu-Cr catalyst.

INTRODUCTION

Commercially, fatty acids or their simple esters are hydrogenated in the presence of copper-chromite catalysts to unsaturated long chain alcohols even though products from this type of reduction can vary widely depending upon reaction conditions (1). Common side reactions include isomerization and saturation of olefinic bonds (2), hydrogenolysis of the alcohols to hydrocarbons (3), alcoholysis of simple esters, and combination of intermediates to produce long chain wax esters (1,4). These reactions can be summarized, as follows:

$RCOOR' \qquad RCH_2OH + R'OH$



$$R-\overset{H}{C}=\overset{H}{C}-R \qquad R-\overset{H}{C}=\underset{H}{C}-R \quad \text{or } R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-R$$

$ROH \rightarrow RH + H_2O$

$RCOOR' + R''OH \rightarrow RCOOR'' + R'OH$

$RCHO + R'CHO \rightarrow RCOOCH_2R'$

or

$R'COOCH_2R$

Similar transformations occur during hydrogenation of triglycerides, but these have been studied in less detail, perhaps because economics favor splitting before hydrogenation, thereby permitting isolation of glycerol, which would otherwise be expected to undergo hydrogenolysis to either 1,2-propanediol or isopropyl alcohol (3,5,6) or both and to their corresponding esters.

In preparing long chain wax esters from crambe oil, essentially an α,α'-dierucoyl triglyceride (7), by hydrogenation on cadmium-promoted copper-chromite, we encountered trace constituents whose structures indicate that the degradation of glycerol to an n-propyl moiety is favored. Hydrocarbons and other by-products of hydrogenation also were identified.

EXPERIMENTAL PROCEDURES

Materials

Crambe oil was from a single batch that had been alkali refined. Fatty acid composition, as determined by gas liquid chromatography (GLC) of methyl esters (8), and expressed as GLC area percent was as follows: 0.1%, C14:0; 2.2%, C16:0; 0.2%, C16:1; 1.0%, C18:0; 18%, C18:1; 11%, C18:2; 7.7%, C18:3; 0.4%, C20:0; 2.4%, C20:1; 0.7%, C20:2; 3.1%, C22:0; 52%, C22:1; 0.5%, C22:2; and 0.1%, C24:1.

Catalysts were Girdler (Chemetron Corp., Louisville, Ky.) T-988 (16%, copper; 25%, cadmium; and, 32%, chromium) and T-1057 (40.8% CuO, 19% CdO, 14.3% Cr_2O_3) both in powder form.

Esters for comparison with unknowns were prepared by refluxing stearic or erucic acid in an excess of the appropriate alcohol containing 1% sulfuric acid.

Hydrogenation

A 1 liter MagneDash stainless steel hydrogenation bomb (Autoclave Engineers, Erie, Pa.) charged with 700 ml crambe oil and 35 g catalyst was flushed with hydrogen to remove air, pressurized to 2000 psig with hydrogen, and heated rapidly to 300 C. Hydrogen pressure then was increased to 3000 psig, and the bomb was maintained at this pressure and 300 C for 5 hr. Following one such hydrogenation with T-988 catalyst, condensable vapors were collected for analysis by venting the head gas through a dry ice-ethanol cold trap.

Analytical Methods

Preparative thin layer chromatography (TLC) was on 1 mm layers of Silica Gel G (Brinkmann Instruments, Des Plaines, Ill.); development was with benzene containing 1% acetic acid. Components visualized under UV light after 2',7'-dichlorofluorescein spray were scraped from the plates and extracted into ACS-grade ether. Analytical-scale TLC was on 0.275 mm layers as described above, except materials were visualized by exposure to iodine vapor.

Hydrocarbons and esters were analyzed by GLC in a Packard 7401 gas chromatograph (Packard Instrument Co., Downers Grove, Ill.) equipped with two glass columns and flame ionization detectors. One column (4 ft x 1/4 in.) was packed with Apiezon L and the other (12 ft x 1/4 in.) with LAC-2-R 446. The liquid phases were coated (5% by wt) on Chromosorb W-AWDMCS (Applied Science Laboratory, State College, Pa.). Peak areas were measured by electronic integration (CRS-11AB/H/40-TS, Infotronics Corp., Houston, Tex.). Gas chromatography-mass spectrometry

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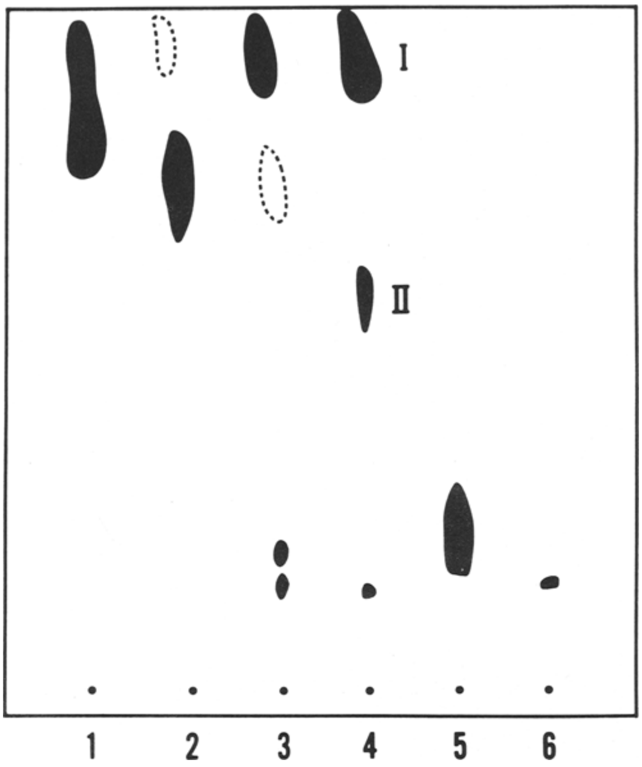

FIG. 1. Thin layer chromatogram of fractions from hydrogenated crambe oil on Silica Gel G; acidic benzene development: 1. fraction A, 2. fraction B, 3. hydrogenation product (T-988 catalyst), 4. sperm whale oil, 5. oleyl alcohol, 6. oleic acid, I wax esters, and II triglycerides. Dotted outlines indicate faint spots.

(GC-MS) used a Packard 7401 chromatograph with a 6 ft x 1/4 in., 5% Apiezon L column coupled to a CEC 21-492-1 mass spectrometer (E.I. duPont de Nemours & Co., Wilmington, Del.) which was operated at a source temperature of 200 C. Scans from m/e 50-600 were taken at 2 sec/decade at the apexes of peaks as determined from the total ionization monitor.

Short chain free alcohols were analyzed by GLC on stainless steel columns packed with Poropak Q (Applied Science Laboratory). For GLC only, a 9 ft x 1/8 in. column was operated at 150 C in an Aerograph A-700 Autoprep gas chromatograph (Varian Associates, Instrument Division, Palo Alto, Calif.) which had a thermal conductivity detector. Peak areas were measured by triangulation. For GC-MS and for analysis of polyols, a 6 ft x 1/4 in. column was used with instrumentation, as described above for GC-MS, and column temperature varied to suit the material analyzed.

RESULTS AND DISCUSSION

Wax esters and long chain acids and alcohols were the principal products from hydrogenation of crambe oil in the presence of either commercial catalyst. Relative amounts of these products were nearly identical, regardless of catalyst, and can be estimated from TLC spot intensities (Fig. 1). Their detailed analysis and evaluation as sperm oil replacements will be presented in another paper. Each hydrogenation mixture, however, also contained unidentified materials, which upon TLC migrated between triglycerides and long chain wax esters when compared with sperm whale oil (9) (Fig. 1). Similar TLC patterns were observed from several different preparations; two samples (a T-988 and a T-1057 catalyzed product) selected for further analysis were considered typical. Two fractions were isolated from each hydrogenation mixture by preparative TLC; one (fraction A) included the wax ester product; the other (fraction B), amounting to less than 5% of the hydrogenation mixture, contained the unknown secondary products. Characterization of materials in these two fractions in terms of their equivalent chain length (ECL) (10,11) characteristics by GLC showed that fraction A contained, in addition to the expected waxes, compounds that were neither long chain wax esters nor known simple fatty acid esters. From ECL values, fraction B appeared to contain some methyl esters, but most components were not identifiable from GLC data. Further analysis by GC-MS, however, established the identities of more than 90% of the secondary products in these two fractions. Short chain alcohols also were identified in the hydrogenation mixtures, although they were not isolated by TLC.

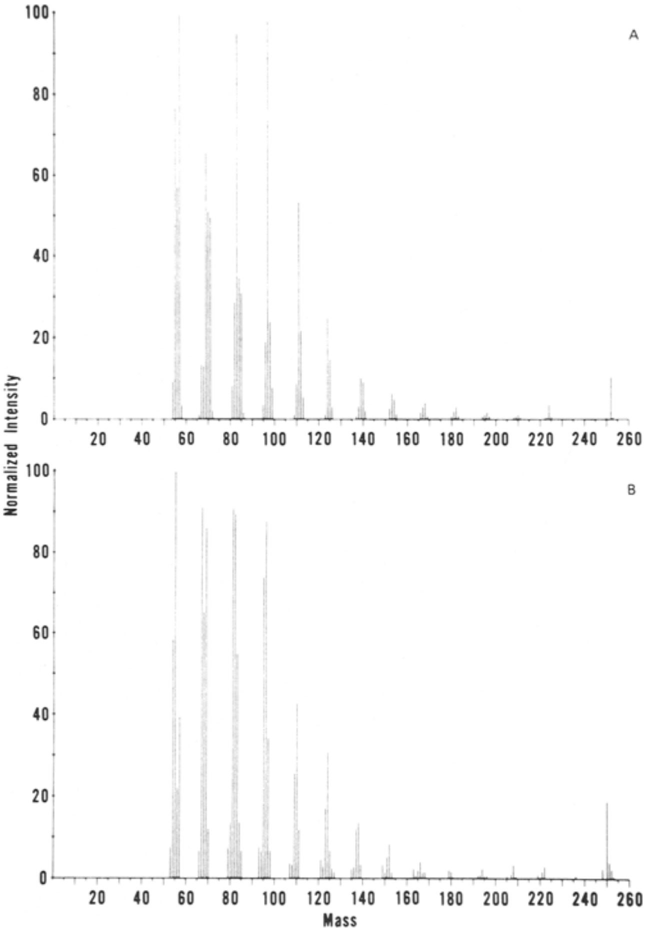

FIG. 2. Mass spectra of (A) 1-octadecene and (B) C_{18} hydrocarbon components from hydrogenation of crambe oil with Cd-Cu-Cr catalyst (T-988).

Hydrocarbons

Under GLC conditions which did not cause elution of long chain wax esters, fraction A yielded a series of compounds thought to be hydrocarbons on the basis of their ECL characteristics and mass spectra. On the basis of peak areas as related to sample size, these materials constituted less than 1% of the total hydrogenation mixture.

Compared in Figure 2 are mass spectra of 1-octadecene and a C-18 component of fraction A, which contained materials that had ECLs identical to those of 1-octadecene, 15.2 on Apiezon L and 12.1 on LAC-2-R 446, when methyl esters of n-alkanoic acids were used as standards. The patterns, which have major ion populations at 14 mass unit intervals, are consistent with hydrocarbon degradation. A difference of 2 mass units between the principal molecular ions in the two spectra and ion-intensity differences, especially for C_6 and larger fragments (m/e > 83), suggest

TABLE I

Hydrocarbons from Catalytic Hydrogenation of Crambe Oil

Equivalent chain length		Area percent by gas liquid chromatography[a]		Identification by gas chromatography-mass spectrometry
Apiezon L	LAC-2-R 446	T-998	T-1057	
13.4	10.8	4	4	16:2
14.1	11.3	2	2	17:1
15.0	12.7	17	24	18:2
15.2	12.1	10	---	18:1
16.0	13.1	4	---	19:1
16.9	14.7	3	3	20:2
17.2	14.0	5	---	20:1
17.9	15.7	5	4	21:2
18.2	15.2	3	---	21:1
18.9	16.8	29	47	22:2
19.3	16.2	13	8	22:1
20.4	---	Trace	Trace	23:1
20.9	18.7	1	1	24:2
21.2	---	Trace	Trace	24:1

[a]These fractions made up less than 1% of the reaction mixture and contained, respectively, 4% (T-988) and 7% (T-1057) of unidentified components. Both catalysts contained cadmium–copper–chromium.

TABLE II

Composition of Short Chain Alcoholic Ester Fractions (Fraction B)

Equivalent chain length		Area percent by gas liquid chromatography[a]		Identification by gas chromatography-mass spectrometry
Apiezon L	LAC-2-R 446	T-988	T-1057	
16.0	16.0	0.4	1	me-16:0
16.8	16.3	1	0.3	et-16:0
16.9	17.6	1.1	0.2	ald-18:1
17.2	17.3	0.8	0.6	ald-18:0
17.7	18.4 19.0	4.0	12	me-18:1 me-18:2
18.0	18.0	1.5	1.2	me-18:0
18.3	18.7 19.1	3.5	6	et-18:1 et-18:2
19.3	19.6 20.0	12	12	np-18:1 np-18:2
19.6	19.2	4	3	np-18:0
20.3	20.7	0.7	1	et-20:1
20.8	21.9	5	2	ald-22:1
21.2	21.6	2	1	np-20:1
21.7	22.4	9	26	me-22:1
22.0	22.0	1	1	me-22:0
22.3	22.7	8	8	et-22:1
22.4	22.3	2	1	ip-22:1
22.6	22.4	1	0.2	et-22:0
23.2	23.5	30	19	np-22:1
23.6	23.2	5	1.6	np-22:0

[a]These fractions made up ca. 5% of the reaction mixture and contained 8% (T-988) and 3% (T-1057) of unidentified components.

[b]me = methyl ester, et = ethyl ester, np = n-propyl ester, ip = isopropyl ester, and ald = aldehyde.

that the C_{18} component of fraction A is a mixture of hydrocarbons, primarily C-18:2 with lesser amounts of C-18:1 and C-18:3. Such analogues were not resolved fully under the conditions of GC-MS, owing to peak spreading in the transfer line, but compounds with ECLs predicted for analogous dienes (10) were detected by analytical GLC, as were higher and lower homologues, whose identities were confirmed by GC-MS. Presumably most of the hydrocarbons in Fraction A arose by elimination of water from saturated or monoenoid alcohols (Table I). The persistence of olefins and the absence of saturated hydrocarbons in the hydrogenation mixtures is additional evidence of the recognized tendency of cadmium to protect isolated double bonds during Adkins-type reductions (2,4).

Esters

Compositions of fraction B from reactions catalyzed by T-988 and T-1057 are given in Table II. Analyses by GC-MS confirmed the presence of methyl esters of crambe fatty acids, which were suspected on the basis of ECL data. This unequivocal identification of methyl esters led readily to other structural assignments. Confirmed similarly were materials that had retention characteristics of ethyl esters, i.e. ECL values 0.7 and 0.3 unit greater than those of the corresponding methyl esters on Apiezon L (12) and LAC-2-R 446, respectively. Ethyl stearate gave ECLs of 18.7 and 18.3 on the respective columns.

Major components that emerged even later than the ethyl esters, at +1.6 ECL units on Apiezon L and +1.2 units on LAC-2-R 446 (compared to methyl esters) were assumed to be isopropyl esters in keeping with the reported quantitative conversion of glycerol to isopropyl alcohol in an Adkins-type hydrogenation of trilaurin (3). Contrary to

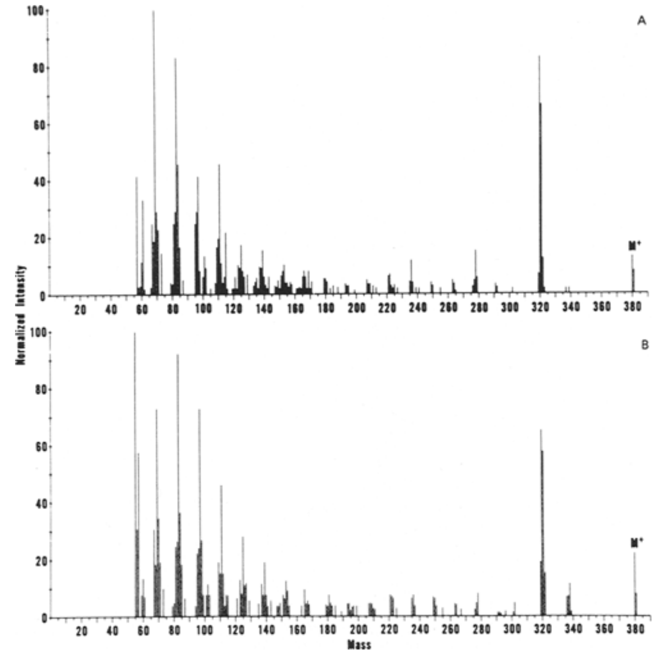

FIG. 3. Mass spectra of (A) n-propyl and (B) isopropyl erucates.

expectations, however, these unknowns were shown to be n-propyl esters by comparison to pure isomeric propyl esters of stearic and erucic acids, which had retention characteristics that were sufficiently different to allow assignment. ECL values for the n-propyl esters and isopropyl erucate are given in Table II. Corresponding values for isopropyl stearate on Apiezon L and LAC-2-R 446 were 18.8 and 18.1, respectively.

The isomeric propyl esters also were differentiated by GC-MS (Fig. 3), even though resolution was somewhat poorer than that achieved under conditions for GLC alone. Compared to n-propyl erucate, the isopropyl ester tends to exhibit a more intense group of ions (m/e 336-339) representing the erucoyl group ± 1 or 2 hydrogen atoms (13). Other major differences, which are not so readily identified, occur at m/e 55 and 56, where isopropyl erucate gives rise to intense ions not present in the spectrum for the n-propyl ester.

Spectra were obtained for almost all components from fraction B of each hydrogenation mixture and confirmed structures assigned on the basis of ECL data. Not more than 1-2% of fraction B from either preparation could be attributed to the isopropyl ester of erucic acid (Table II), and no other isopropyl esters were found. These may have been present at levels too low for identification as also may have been true for other expected products: methyl eicosenoate, ethyl stearate, and n-propyl palmitate.

Aldehydes

Three minor GLC peaks that apparently represented C_{18} and C_{22} compounds had ECL values (14) and mass spectra that best fit aldehydes. Their spectra, which confirmed the assumed chain lengths, were characterized by loss of 18 (water) and 29 (formyl) atomic mass units from the molecular ions, as it typical of aldehydes. Certainly, aldehydic intermediates are to be expected in Adkins-type reductions (1), and they are known to occur during wax ester synthesis by dehydrogenation of alcohols over copper-zinc catalysts (15). Our analyses (Table II) indicate that they are among the least prevalent species.

Alcohols

Finding methyl and ethyl esters and the preponderance of n-propyl esters, instead of anticipated evidence of either isopropyl alcohol or 1,2-propanediol, prompted a thorough search for volatile constituents and unesterified short chain alcohols in the reaction mixture and head gas from the T-988 hydrogenation. Condensate from the head gas (1-2 ml of clear liquid) was analyzed by GLC on a Poropak Q column operated under conditions that optimized separation of plausible components. Water, methanol, acetaldehyde, ethanol, acrolein, isopropyl alcohol, allyl alcohol, and n-propyl alcohol all were separated with excellent resolution from propanal and acetone, which had identical retention times. The head gas condensate consisted of 75% water, 6% methanol, 6% ethanol, 4% isopropyl alcohol, and 9% n-propyl alcohol. Analysis of low boiling constituents (<1%) of the hydrogenation mixture under the same conditions showed 32% water, 0.6% methanol, 4.0% ethanol, 12% isopropyl alcohol, and 51% n-propyl alcohol. These values, which are uncorrected for detector response, reflect only relative peak areas. However, when mixtures containing equal amounts of standard compounds were analyzed, the ca. equal peak areas indicated a direct correlation between area and wt.

TABLE III

Ratios of C_{18}/C_{22} Acyl Groups in Constituents of Crambe Oil and Hydrogenation Products

	Catalyst	
Constituent	T-988	T-1057
Crambe oil acids	0.68	0.68
Aldehydes	0.38	0.40
Hydrocarbons	0.64	0.44
Total esters	0.44	0.60
Methyl esters	0.55	0.49
Ethyl esters	0.39	0.73
n-Propyl esters	0.46	0.73
Isopropyl esters	0	0

Much of the water in the trapped vapor may have been condensed atmospheric moisture, since the molar ratio of water to n-propyl alcohol (28:1) in the condensate is far greater than would be expected from the ratio of these same constituents in the hydrogenation mixture (2:1). With the exception of n-propyl alcohol, relative molar concentrations of the alcohols in the head gas were in keeping with their bp. Molar ratios, n-propyl alcohol:isopropyl alcohol, in the head gas and in the hydrogenation mixture were 2:1 and 4:1, respectively.

Among polyols that might have been generated during the hydrogenation, only a trace of 1,2-propanediol was found in the hydrogenation mixture, even though the condensed head gas and liquid product both were analyzed under conditions adequate to resolve and detect glycerol, 1,2-propanediol, and 1,3-propanediol.

Comparison of Catalysts

Product mixtures generated by the two catalysts were similar qualitatively but substantially different quantitatively. The tendency of T-988 to promote olefin reduction, which gave rise to monoenoid hydrocarbons (Table I) and to a lesser extent saturated esters (Table II), was an unexpected result considering that the higher concentrations of cadmium in T-988 (T-988, cadmium = 0.22 moles/100 g, copper-cadmium = 1.1; T-1057, cadmium = 0.15 moles/100 g, copper-cadmium = 3.3) should have afforded greater protection against saturation (2,4).

The T-988 catalyst also appeared to promote chain shortening to a greater extent than did T-1057 (Table I), but the relative concentration of methyl esters in the T-988 ester fraction was less than half that in the ester mixture from the T-1057 reaction (Table II). Apparently C_1 fragments released from long chain constituents contributed little if any to methyl ester formation. n-Propyl esters were favored over methyl esters in the T-988 reaction, and both catalysts produced ethyl esters in ca. the same proportions.

Additional differences in catalyst selectivity are apparent when the two reaction mixtures are compared in terms of C_{18} and C_{22} constituents (Table III). With T-988, all secondary products had smaller C_{18}:C_{22} ratios than the starting oil. With T-1057, however, only hydrocarbons, aldehydes, and methyl esters had smaller ratios; ethyl esters and n-propyl esters actually were enriched in C_{18} acids relative to C_{22}.

Product variations easily might be due to differences in either catalyst composition or preparation, or both. The two catalysts were prepared in different ways (E.W. Black, Chemetron Corp., Louisville, Ky., personal communication). Water suspensions of T-988 and T-1057 were, respectively, slightly acid (pH 6.1) and slightly basic (pH 7.6). It is, therefore, tempting to attribute some of the different results produced by these catalysts to differences in their acid base characteristics.

Reaction Course

If the inherent variability of Adkins-type catalysts, the multiplicity of products, and the limits of our analyses are considered, visualizing the reduction of crambe oil in terms of a single simple reaction sequence would be inappropriate. However, detailed analysis of products from the known triglycerides allows insight into initial events that contribute to the process and that might, therefore, be amenable to control. In particular, three characteristics of the secondary products are especially noteworthy: the preponderance of n-propyl, instead of isopropyl esters, the general enrichment of C_{22} constituents, and the fourfold predominance of n-propyl alcohol over isopropyl alcohol in the reaction mixture. These conditions all suggest that elimination of β-substituents of the triglycerides is the first significant transformation of the oil and that it proceeds rapidly compared to the liberation of α-C_{22} moieties. Conceivably, dierucoyl triglycerides might assume an unusual conformation on the catalyst and, thereby, favor elimination at the β-position, but it remains to be seen to what extent the course of the reaction is actually a consequence of the unusual structure of crambe oil.

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