The Acid-Catalyzed Addition of Alkoxyl Groups to the Olefinic Double Bonds of Soybean Oil[1]

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The acid-catalyzed reaction of soybean oil with the homologous series of straight-chain alcohols: methyl, ethyl, n-propyl, n-butyl and n-hexyl in a pressurized system yielded completely transesterified products and 18–31% substituted alkyl ethers. Mass spectrometry of the hydrogenated methyl ester derivatives showed that the addition reaction occurred at one of three double bonds of the unsaturated fatty acids. The reaction with three secondary alcohols yielded only 0.1–2.5% substituted alkyl ethers.

One of the main objectives of our research is to modify physical-chemical properties of vegetable oils to make them more suitable as alternative or emergency fuels for direct-injection, farm tractor diesel engines. Unmodified vegetable oils are not suitable fuels for such engines, mainly because of their high viscosities. Converting vegetable oils to esters of short-chain monohydric alcohols has partially overcome the difficulties associated with high fuel viscosity and low vapor pressure when these oils are used as fuels in diesel engines (1).

The esters can be modified further by taking advantage of the reactivity of the double bond system in unsaturated fatty materials. Some of the reactions considered had been applied to simple olefins in the petrochemical industry, but they apparently had not been investigated for the more complex unsaturated systems in fats and oils.

The addition of primary alcohols to olefins is well known. Reychler (2) heated trimethylethylene (2-methyl-2-butene), methanol and sulfuric acid together in a sealed tube and found the product to be methyl t-amyl ether. Later, Evans and Edlund (3) prepared a series of tertiary alkyl ethers by the reaction of either trimethylethylene or isobutylene (2-methyl propene), the latter hydrocarbon having terminal (vinyl) unsaturation, with primary and secondary alcohols in the series methyl through butyl.

Since that time, research interest has been directed almost exclusively toward terminally unsaturated olefins. Reactions studied include that of isobutylene and methanol, catalyzed by acidic ion-exchange catalysts (4,5), methane sulfonic acid (6), macroporous sulfonic acid resins (7), Lewis acids (8), and lithium perchlorate (9). No literature references could be found in which the substrate was a long-chain, nonvinyl, olefinic hydrocarbon, fatty acid or ester. Because reaction appeared feasible, this study was undertaken.

MATERIALS AND METHODS

Soybean oil. Soybean oil used was a refined and bleached oil.

Reagents. Methanol, absolute ethanol, 1-propanol, 2-propanol, 1-butanol, 1-hexanol, 2-hexanol and 2-octanol were obtained from commercial sources and stored over molecular sieves (Linde, 4A) prior to use.

Reference materials. Methyl elaidate was prepared from elaidic acid (Nu-Chek Prep, Elysian, Minnesota) by boron trifluoride-catalyzed methanolysis (10,11). Methyl esters of soybean oil were prepared by transesterification with 5% anhydrous HCl-MeOH.

Reaction of soybean oil with methanol. (Preliminary trials). Soybean oil (2.0 g), methanol (15 ml) and 0.5 ml concentrated sulfuric acid were placed in a 25-ml Teflon-lined Parr 4745 Acid Digestion Bomb (Parr Instrument Co., Moline, Illinois). In a series of runs, the bomb and contents were heated 12–36 hr in an oven at temperatures ranging from 100 to 140 C.

At the end of each reaction period, the bomb was allowed to cool to room temperature, chilled in a refrigerator to 0 C and then opened. The contents were transferred to a separatory funnel, diluted with 500 ml water and extracted with five 100-ml portions of diethyl ether. The ether solution was rinsed with water to remove the acid catalyst. After drying over anhydrous sodium sulfate, the ether was removed by distillation under reduced pressure in a rotary evaporator with the temperature maintained at 40 C.

Reaction of soybean oil with longer-chain alcohols. Soybean oil and sulfuric acid in the quantities noted above were placed in the digestion bomb with 15 ml of the respective alcohol. The bomb and contents were heated 19 hr in the oven at 140 C. The products were worked up as described for the reaction with methanol.

Thin layer chromatography (TLC). Analytical TLC of the reaction products was carried out on precoated Silica Gel 60F-254 plates (E. Merck, Darmstadt, Germany) (0.25 mm thick) with the solvent system hexane/ethyl ether (70:30, v/v). Components were visualized by charring with sulfuric acid/dichromate.

Gas liquid chromatography (GLC). GLC of the reaction products was carried out on an instrument equipped with FID detectors by using a 60-m × 0.24-mm fused silica capillary column coated with the polar phase SP-2340 (Supelco, Inc., Bellefonte, Pennsylvania). The flow rate of the helium carrier gas was 2–4 ml/min. Pressure was maintained at 140 kilopascals (KPa). Methyl esters of the hydrogenated reaction products were analyzed on a 10-m × 0.32-mm fused silica column coated with the nonpolar phase SE-30 (Supelco, Inc.). The helium flow rate was 1–2 ml/min at 25 KPa. Detector and injector temperatures were held at 250 C. In all runs, temperature was programmed 180–250 C at 3 C/min and held at the maximum temperature for 10 min. Methyl esters were identified by their Equivalent Chain Length (ECL).

Infrared (IR) spectra. IR spectra were recorded in 1% CS_2 solutions in 1-mm NaCl cells.

Hydrogenation. For certain analyses, reaction products (ca. 50 mg) were hydrogenated in hexane four hr at ambient temperature and atmospheric pressure with palladium-charcoal (10%) catalyst. The catalyst was removed

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by filtration, and the product was isolated by evaporating the solvent.

Preparation of methyl esters. The hydrogenated products were converted to methyl esters by saponification followed by boron trifluoride-catalyzed methanolysis (10,11).

Gas chromatography-mass spectrometry (GCMS). The hydrogenated methyl esters were chromatographed in a 12-m × 0.2-mm HP-7 capillary GC column. Temperature was programmed 180–250 C at 3 C/min. The inlet temperature and transfer line were held at 250 C. The detector was a Hewlett-Packard 5970 Mass Selective Detector. Scanning was conducted from 40–550 daltons at 0.84 scans/sec (1.2 sec/scan).

RESULTS AND DISCUSSION

GLC analyses of the reaction products obtained at varying times and temperatures indicated that optimum reaction conditions were achieved at 140 C and 19 hr reaction time. In accordance with the bomb manufacturer's instructions, temperatures above 140 C were avoided because of the thermal limitations of the Teflon liner.

GLC data of the reaction products with primary alcohols are shown in Table 1. GLC and TLC showed that in all cases, complete conversion from the triglycerides to the corresponding alkyl esters of the fatty acids was attained. The gas chromatograms showed the expected peaks for the corresponding alkyl palmitates (ECL 16.0, ECL based on retention time of esters of the respective alcohols), stearates (ECL 18.0), oleates (ECL 18.5), linoleates (ECL 18.9), linolenates (ECL 19.5), and in addition they showed a cluster of new peaks at ECL 21.3–22.8. These peaks were alkoxyl-branched alkyl esters and were due to saturated derivatives, such as the product of the addition to the oleate chain, and to unsaturated products, which could result from addition to one double bond (δ-9 or δ-12) of linoleate or to one or two double bonds (δ-9, -12 or -15) of linolenate.

TABLE 1

Gas Liquid Chromatography (GLC)[a] of Alkoxy Adducts

Alkyl ester products	Soybean methyl esters[c]	Alcohols used[b]				
		Methyl	Ethyl	1-Propyl	1-Butyl	1-Hexyl
16:0	10	12	14	13	12	15
18:0	4	5	6	5	5	9[d]
18:1-t	0	3	3	8	8	
18:1-c	22	19	23	14	2	23
18:2-"t"[e]	0	3	2	15	7	10
18:2-c-c	57	34	31	22	23	17
18:3	7	3	2	1	2	2
18-OR[f]	0	21	18	31	31	25

[a] Polar column 60-m × 0.24-mm capillary, SP-2340. Programmed 180–250 C, 3 C/min. Area percent.

[b] 2-Propyl, 2-hexyl and 2-octyl alcohols were also used, but reaction products showed no more than 2.5% adducts on GLC and are not summarized here.

[c] These data show the composition of the unreacted mixed methyl esters.

[d] GLC peaks overlapped.

[e] "t" refers to any linoleates with a *trans* double bond whether *c-t*, *t-c* or *t-t*.

[f] Total adducts whether saturated or unsaturated.

GLC of the products of reaction with the secondary alcohols indicated transesterification but little addition to the double bonds. Reaction with 2-propanol resulted in only 1.3% of an adduct as contrasted to 31% with 1-propanol. The gas chromatograms of the 2-hexyl and 2-octyl reaction products similarly showed only 0.1% 2-hexyl adducts and 2.5% 2-octyl adducts.

Elaidinization is a side effect and is the result of isomerization of a *cis* double bond in the oleate or linoleate chain. The identity of the elaidate (18:1-t) peak on GLC was confirmed by GLC of an authentic sample of methyl elaidate. The elaidate absorption at 10.3 μm (12) was observed on IR of the reaction products. It is not readily apparent whether or not the *trans* double bonds have an effect on the adduct formation.

To locate the added side chains by mass spectrometry without interference from isomerization or fragmentation of double bonds, we hydrogenated the reaction products. The adducts along with the remaining nonadducted fatty acids subsequently were shown by GLC to be in the form of saturated alkyl esters derived from the alcohol used in the reaction. This resulted in higher retention temperatures and times than would be expected with methyl esters. Therefore, we converted these alkyl esters to methyl esters by methods which were not expected to affect the alkoxyl side chain. Sequential hydrogenation, saponification and reaction with BF_3-MeOH converted the adducts and original fatty acid alkyl esters to their corresponding saturated methyl esters.

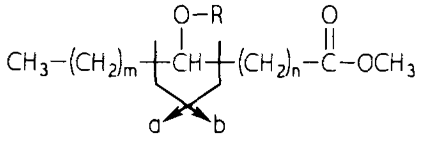
Comparison of the resulting gas chromatograms with the chromatograms of hydrogenated soybean oil methyl esters easily confirmed the presence of methyl palmitate and methyl stearate accompanied by the disappearance of the alkyl oleate, elaidate, linoleate and linolenate peaks. For each product, the cluster of peaks previously attributed to saturated and unsaturated adducts now appeared as a major peak with a small shoulder. ECL's (based on methyl esters) of the major peaks are shown in Table 2.

Ryhage and Stenhagen (13) showed that alkoxyl-substituted methyl octadecanoates exhibit characteristic MS cleavages. Principal peaks are observed for cleavages on either side of the carbon on which the alkoxyl group is substituted (Table 2, ions a and b). Masses of the identifying ions that were observed are summarized in Table 2. No molecular ions were found, but all samples showed an ion corresponding to M-31.

The products from all of the primary alcohols gave ions indicating alkoxyl addition at carbons 9 and 10. These are the products expected from nonspecific alkoxylation to either side of the 9–10 double bonds of either oleic, linoleic or linolenic acids. The products from reaction with methanol and with 1-butanol also showed ions resulting from alkoxylation at either side of the 12–13 double bonds of linoleic or linolenic acids. The mass spectrum of the hydrogenated methyl esters of the reaction product with 1-propanol showed the expected ions indicating alkoxyls at the 9- and 10-positions and in addition gave ions indicating substituents at carbons 12 and 15. No ions were found which indicated alkoxyls at carbons 13 or 16, although these would be expected. GLC of the reaction products showed some minor peaks with retention times

TABLE 2

Mass Spectrometry of Hydrogenated Alkoxy Methyl Esters[a]



$CH_3-(CH_2)_m-CH(O-R)-(CH_2)_n-C(=O)-OCH_3$

m + n = 15

				Mass spectral data										
				9[b]		10		12		13		15		
R	ECL[c]	Mol wt[d]	M-31	a	b	a	b	a	b	a	b	a	b	
CH_3-	19.2	328	297[e]	171	201	157	215	129	243	115	257	[f]		
CH_3-CH_2-	19.5	342	311	185	215	171	229							
CH_3-$(CH_2)_2$-	20.3	356	325	199	229	185	243	157	271			115	313	
CH_3-$(CH_2)_3$-	21.2	370	339	213	243	199	257	171	285	157	299			
CH_3-$(CH_2)_5$-	22.8	398	367	241	271	227	285							

[a] See (13).

[b] Carbon to which the alkoxyl group is attached.

[c] Equivalent chain length based on retention time of known methyl esters on nonpolar column.

[d] Calculated mol wt.

[e] m/z. Data is given when the observed ions were the same as the calculated values.

[f] Mass spectral data is omitted when no ions were found which corresponded to the calculated values.

greater than those of the saturated and unsaturated adducts as did GLC of the hydrogenated methyl esters, but MS gave no conclusive evidence of their identities or indication that two or more alkoxyl groups had been added to the chain.

Further investigation is underway to determine what properties of the ether-esters are exploitable for industrial products. The alkoxyl group can serve the purpose of altering the hydrocarbon chain linearity, thus altering viscosity. It might also decrease the reactivity of the chain with oxygen at high temperatures, and because there are fewer double bonds, the chain would be less subject to oxidative polymerization and cross-linking reactions. It would appear that such products from unsaturated fatty materials might have enhanced properties with regard to lubricants, cosmetics, fuel additives and alternative fuels.

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