Selective Conjugation of Soybean Esters to Increase Hydrogenation Selectivity

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ABSTRACT

Polyunsaturated fatty acid methyl esters of soybean oil (MeSBO) were selectively conjugated as a means of increasing the linolenate selectivity of various homogeneous and heterogeneous hydrogenation catalysts. Kinetics of the conjugation reaction in various solvents indicated that linolenate conjugated 5-8 times faster than linoleate. Selective conjugation of MeSBO with potassium *t*-butoxide in dipolar solvents resulted in an increase in linolenate hydrogenation selectivity to 7-8 with Ni and Pd heterogeneous catalysts, and to 7-10 with homogeneous and heterogeneous chromium carbonyl catalysts. *Trans*-unsaturation in the hydrogenated products was only 1-3% with the chromium carbonyl catalysts, in contrast to 30-39% with the heterogeneous metal catalysts. Triglycerides were readily converted to partial glycerides and *t*-butyl esters with the potassium *t*-butoxide reagent.

INTRODUCTION

The selective hydrogenation of linolenic acid in soybean oil is one of the most important ways of improving its oxidative and flavor stabilities (1). Commercially employed nickel catalysts have a limited linolenic selectivity (K_{Le}/K_{Lo}) of about 2. Consequently, soybean oil hydrogenated to an iodine value of 110 still contains 3% linolenic acid (2). Lowering the iodine value further decreases the winterized oil yield. In contrast, copper-containing catalysts are highly selective for hydrogenation of linolenic acid (K_{Le}/K_{Lo} = 13-15) but are much less active than nickel catalysts (3).

Heterogeneous catalysts also form higher melting *trans*-isomers, which decrease the winterized oil yield. In contrast, certain homogeneous and heterogeneous chromium carbonyl complexes were found to hydrogenate polyunsaturates to *cis*-monoenes (4-6). Selective conjugation prior to hydrogenation was suggested as an alternate approach to improving the selectivity of homogeneous catalysts (7). Since both nickel and palladium heterogeneous catalysts preferentially reduce conjugated esters over unconjugated esters (8), selective conjugation of soybean esters prior to hydrogenation was expected to enhance the selectivity.

Conjugation reaction is of great importance in industry as well as in the laboratory. Conjugation of polyunsaturated fatty acids improves the drying properties of vegetable oils. Conjugation with alkali in ethylene glycol forms the basis for estimating polyunsaturated fatty acids (9). Potassium *t*-butoxide (KtBuO) in *t*-butanol was suggested as a better reagent (10) that conjugated at lower temperatures. Strong bases such as KtBuO, in the presence of dipolar aprotic solvents such as tetraethylene glycol dimethyl ether (tetraglyme), are capable of catalyzing conjugation much more rapidly even at room temperature (11). More recently, DeJarlais et al. (12,13) successfully conjugated soybean and linseed oils with sodium and potassium salts of dimethyl sulfoxide. In this paper, we report kinetic studies of the selective conjugation of methyl linolenate in soybean esters. Homogeneous and heterogeneous chromium carbonyl and heterogeneous nickel and palladium catalysts were then used to selectively hydrogenate the conjugated esters.

[1]Presented at the AOCS North Central Section Symposium, March 1980.

EXPERIMENTAL

Materials

All solvents were freed of peroxides by distillation over sodium metal or calcium hydride. Potassium tertiary butoxide (97%) was obtained commercially. Soybean oil methyl esters were prepared with sodium methoxide catalyst and distilled under vaccuum after washing with sodium bicarbonate. Ni catalysts (G-15-Girdler catalyst) and Pd catalyst (0.2% Pd-on-Al_2O_3-Englehard Industries) were obtained from commercial sources. The preparation of chromium carbonyl complexes has been described previously (4-6).

Methods

Selective conjugation. Fifty-two mg of KtBuO was stirred into 5 ml of tetraethylene glycol dimethyl ether (tetraglyme). After centrifugation and cooling to 20 C, 1 ml of solution was titrated with 0.1 N HCl. The remainder was poured into 2 g soybean methyl esters. The solution was maintained at 20 C under N_2 and samples were taken at intervals. Conjugation reactions were performed similarly with other solvents and reagents. A large batch (100 g) of soybean methyl esters was similarly conjugated and used for hydrogenation.

Analysis. The composition of the conjugated esters was determined by a combination of methods. Fatty acid composition was determined by gas liquid chromatography (GLC) with packed columns (EGSS-X). In this system *cis,trans*-conjugated dienes and methyl linolenate are eluted together. Methyl linolenate was, therefore, measured by capillary GLC with polyphenyl ether as the stationary phase (14). The small amounts of conjugated trienes formed are estimated by the official AOCS method (9). The percentage of isolated *trans* was measured by comparing the infrared absorption of methyl esters at 10.36 μm with methyl elaidate standard.

Conjugation. Conjugation selectivity ratios (rate of linolenate conjugation/rate of linoleate conjugation) were determined from the following equation assuming first order reaction.

$$\text{Conjugation selectivity} = \log \frac{Le_o}{Le_t} / \log \frac{Lo_o}{Lo_t},$$

where Le_o = concentration of linolenate at zero time; Le_t = concentration of linolenate at time t; Lo_o = concentration of linoleate at zero time; and Lo_t = concentration of linoleate at time t.

Hydrogenations. Hydrogenation of conjugated esters with Pd (0.2% Pd-on-alumina) and Ni (Girdler-G-15; 25% nickel) catalysts was carried out in a glass manometric apparatus described previously (15). Hydrogenation with chromium carbonyl complexes was performed according to a previously described procedure (4-6). Hydrogenation selec-

tivity ratios were determined with a digital computer (16).

RESULTS AND DISCUSSION

Conjugation of Methyl Esters

The effect of different solvents on the selectivity and reactivity of KtBuO and potassium methoxide was investigated for the conjugation of linolenate in MeSBO. Fig. 1 shows the change in fatty acid composition produced by 0.43 M KtBuO in dimethyl formamide.

Decrease in linoleate was followed by a concomitant increase in conjugated dienes. Decrease in linolenate was accompanied by the formation of two new products: conjugated trienes (CT), and diene-conjugated trienes (CdT-trienes in which two double bonds are conjugated and one double bond is isolated). There was no change in palmitate, stearate or monoene.

The analytical results of the conjugation reaction with several alkaline reagents and solvents are shown in Table I. Of the three solvents used with KtBuO, tetraglyme and diethylene glycol dimethyl ether (diglyme) accelerated the conjugation reaction more easily than did dimethyl formamide (DMF). The relative effectiveness of tetraglyme and diglyme in conjugating MeSBO could not be compared using the data in Table I because of the different molarities of KtBuO employed. When a 0.16 M KtBuO solution in tetraglyme was used, conjugation of MeSBO in 5 min was comparable to that achieved with diglyme in 37 min. It appears, therefore, that tetraglyme is a somewhat more effective solvent than diglyme in catalyzing conjugation. With tetraglyme as solvent, KtBuO is much more reactive than potassium methoxide.

With tetraglyme and DMF, the conjugation reaction occurred with an average linolenate selectivity of 7. The selectivity is lower (K_{Le}/K_{Lo} = 5-6) with diglyme. Potassium methoxide conjugated linolenate in soybean esters with a slightly higher selectivity.

With every solvent or reagent employed, linolenate conjugated preferentially to CdT over CT. When methyl linolenate was completely conjugated with 0.3 M KtBuO in tetraglyme, the CdT to CT ratio was 2.8. According to a stepwise mechansim proposed by Nichols et al. (17), the first step is the formation of four CdT isomers ($\Delta^{9,11,15}$; $\Delta^{10,12,15}$; $\Delta^{9,13,15}$; and $\Delta^{9,12,14}$). In the second step, two of these isomers ($\Delta^{10,12,15}$ and $\Delta^{9,12,14}$) further conjugate to CT. According to this mechanism, nearly equal amounts of CdT and CT should result. Sreenivasan and Brown (10) reported from spectroscopic data that 47.7% CdT and 36.7% CT are formed with 1.3 M KtBuO in *t*-butanol at 95 C. The unusually high proportion of CdT in our reactions may be due to cyclization or polymerization of CT. This possibility is less likely, however, since conjugations were carried out under milder conditions. Among other explanations, the most plausible are that the four CdT isomers are formed at different rates or that the second step is much slower because of the low concentration of alkali used. Structural analysis of the conjugated products is required to test these hypotheses.

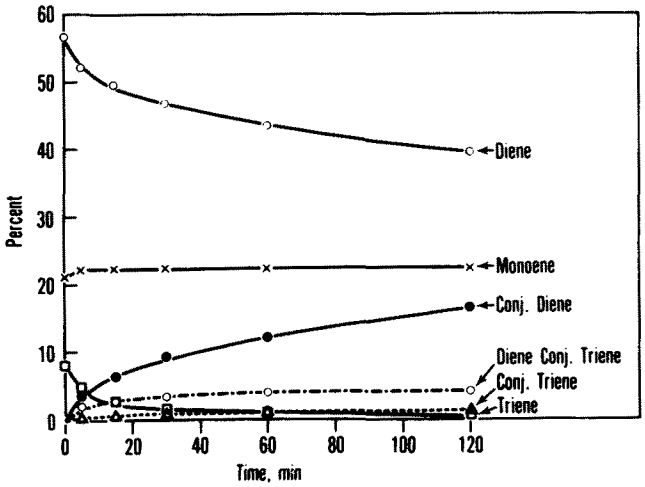

FIG. 1. Change in fatty acid composition during conjugation of MeSBO with 0.43 M potassium *t*-butoxide in dimethyl formamide.

Even though there was 8% linolenate in the original methyl esters, the trienoic esters in the conjugated products amounted to about 7%. This discrepancy is either due to inaccurate methodology or to formation of side-products. During GLC of the conjugated esters, a small peak was observed that eluted just ahead of palmitate. Conjugation of pure methyl linolenate gave two small (unidentified) peaks that eluted just ahead of CdT. Complete hydrogenation of conjugated linolenate esters formed stearate and a small unidentified peak (8%) that preceded stearate during GLC. Complete hydrogenation of partially conjugated esters produced two unidentified peaks that eluted ahead of palmitate and stearate (Fig. 2). These peaks were later identified as *t*-butyl esters of palmitic and stearic acids by gas chromatography-mass spectroscopy (m/e = 57, *t*-butyl ion). With potassium methoxide, no *t*-butyl esters formed and the sum of all the trienes in the conjugated products was still 7% (Table I). It appears, therefore, that the discrepancy was attributable to the analytical methods employed.

By titration, KtBuO was found to be 97% pure. There was 21% weight loss upon evacuation at 0.05 mm. The

TABLE I

Kinetics of Conjugation of Soybean Methyl Esters[a]

	Time (min)													
	0.37 M K *t*-butoxide in dimethyl formamide					0.14 M K *t*-butoxide in diglyme			0.06 M K *t*-butoxide in tetraglyme			0.35 M K methoxide in tetraglyme		
Me ester	0	5	30	60	120	5	15	37	30	60	90	5	15	60
Oleate	21.1	22.3	22.6	22.5	22.5	23.2	23.0	22.4	22.1	21.8	22.5	21.5	21.6	21.5
Linoleate	56.7	52.1	47.0	43.7	39.8	47.2	40.1	30.3	48.9	46.4	39.7	53.9	45.9	26.8
Conj. diene	–	3.9	9.2	12.3	16.6	7.4	14.9	25.5	6.7	9.4	16.4	3.6	10.9	30.5
Linolenate	8.1	4.6	1.8	1.2	0.6	3.2	1.0	0.0	3.3	2.2	0.6	5.0	1.6	0.3
Conj. triene	–	0.5	1.3	1.3	1.4	1.2	2.1	2.4	1.5	2.0	1.8	0.6	2.0	2.1
Diene-conj. triene	–	2.1	3.5	4.1	4.3	2.6	3.8	4.3	3.0	3.6	4.1	1.4	3.4	4.4
K_{Le}/K_{Lo}	–	7	8	7	7	5	6	–	6	7	7	10	8	7

[a]2 g MeSBO, 4 ml reagent at 20 C.

evacuated material now titrated as 117% KtBuO. Apparently, some reagent was hydrolyzed to KOH and *t*-butanol. The evacuated material calculated out as 83% KtBuO and 17% KOH. The evacuated reagent was no longer soluble in tetraglyme, diglyme or DMF. It appears that some *t*-butanol is essential to solubilize the reagent.

Conjugation of Triglycerides

Triglycerides were found to be more resistant to conjugation than methyl esters. After a 2-hr reaction with 0.3 M KtBuO in tetraglyme, there was 3.4% linolenate in the product. Thin-layer chromatography provided evidence of partial hydrolysis to mono- and di-glycerides and formation of significant amounts of *t*-butyl esters (Fig. 3). Apparently the ester linkages are very weak and are susceptible to hydrolysis by the strong alkali. Also, the free *t*-butanol in the reagent transesterified the triglycerides.

Hydrogenation

Both nickel and palladium catalysts hydrogenated conjugated esters with high selectivity (Table II). Had these esters not been conjugated, a selectivity of 2 would have been observed (18). However, these catalysts produced significant amounts of *trans*-isomers. Because of the small scale of these hydrogenations (500 mg esters), the amount of nickel catalyst used was 5 to 10 times as much as is commonly used. However, the linolenate selectivity is not affected by catalyst concentration (19). Cr carbonyl catalysts formed products with virtually no *trans*-isomers (Table III). With different chromium complexes, linolenate selectivity ranged from 7 to 10. This selectivity is higher than the values of 4-5 observed previously without prior conjugation (4). Since both homogeneous and heterogeneous catalysts caused little or no increase in saturates, linoleate selectivity was very high.

When Ben-et et al. (7) treated a 1:1 linoleate-linolenate mixture with KtBuO in tetraglyme, they reported linolenate conjugation of up to 30% with infinite selectivity (no linoleate conjugation). They also reported inconsistent results with the same reagent and a variation in selectivity between 1.3 and 16.5. However, it is not clear how they arrived at their selectivity values since they used a GC method for determining conjugation, which cannot separate linolenate from conjugated diene. Furthermore, they did not test the principle of selective hydrogenation by preconjugation, because all their hydrogenation data were obtained on completely conjugated safflower methyl esters. In contrast, the present study carried out with selectively conjugated soybean esters demonstrated that the linolenate selectivity obtained for hydrogenation was of the same

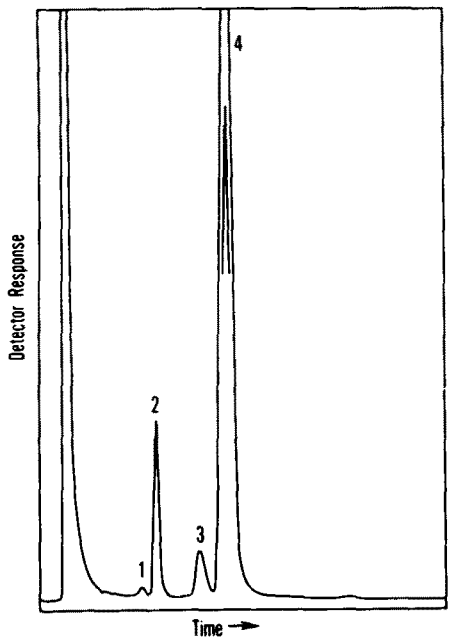

FIG. 2. GLC separation of soybean methyl esters after conjugation and hydrogenation on a 15% EGSS-X on 100/120 Gas Chrom P column: 6 ft × 1/8″ od. Esters separated (1) *t*-butyl palmitate, (2) methyl palmitate, (3) *t*-butyl stearate, (4) methyl stearate.

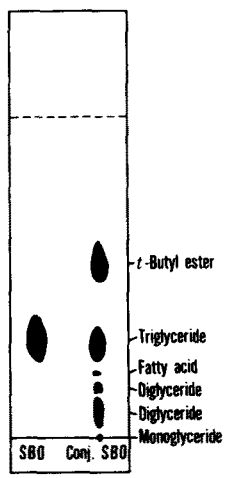

FIG. 3. TLC of conjugated soybean oil. Solvent system: PE:EE:HOAc-90:10:1 (vol).

TABLE II

Hydrogenation of Selectively Conjugated Soybean Methyl Esters with Heterogeneous Nickel and Palladium Catalysts at 160 C

Catalyst	Metal (%)	Time (min)	Fatty acid composition (%)[a] S	M	D(CD)	T	*Trans* (%)	Selectivity K_{Le}/K_{Lo}
None			15.0	22.5	56.1 (16.4)	0.6[b]	–	–
Ni	0.2	39	15.5	48.0	36.5 (2.2)	0.0	30	7[c]
Pd-Al_2O_3	0.002	75	14.7	46.5	38.8 (3.1)	0.0	39	8[c]

[a]S = Saturates; M = monoene; D = diene; CD = conjugated diene; T = triene.
[b]Also 4.1% diene-conjugated triene and 1.7% conjugated triene.
[c]Calculated assuming 0.1% triene.

TABLE III

Hydrogenation of Selectively Conjugated Soybean Oil Methyl Esters[a]

Catalyst	(%)	Temp (C)	Time (hr)	Fatty acid composition (%)[b] S	M	D(CD)	T[c]	Selectivity K_{Le}/K_{Lo}	*Trans* (%)
$Cr(CO)_6$	4	175	6	15.6	44.4	39.8 (0.0)	0.2	8	1
Me benzoate-$Cr(CO)_3$[d]	3	150	6	15.3	47.3	36.9 (0.3)	0.2	7	1
Polystyrene-$Cr(CO)_3$[e]	4	180	6	15.1	40.2	43.4 (1.0)	0.4	9	3
Polystyrene-$Cr(CO)_3$[e]	4	185	6	15.5	39.6	44.4 (0.3)	0.3	10	2
Polyvinyl benzoate-$Cr(CO)_3$[f]	9	160	12	15.1	40.4	43.7 (0.4)	0.4	9	2

[a]At 500 psi H_2 in 150-ml Magne Dash autoclave containing 10 g esters and 40 ml cyclohexane.

[b]S = saturates; M = monoenes; D = dienes; CD = conjugated dienes; T = trienes.

[c]Determined by alkali-isomerization method.

[d]1% Crosslinked with divinyl benzene; 9.1% Cr.

[e]Macroreticular highly crosslinked; 6.4% Cr.

[f]8.0% Cr.

order as that obtained for conjugation. Selective conjugation of linolenate is, therefore, the key step in the increased hydrogenation selectivity. The agreement between linolenate selectivity obtained after conjugation and hydrogenation provides further confidence in our methodology.

The results of this study support the previous mechanistic hypothesis that conjugation of polyunsaturated fatty acids is necessary to achieve hydrogenation selectivity with both homogeneous and heterogeneous catalysts (20). These results are also consistent with the high selectivity of copper catalysts (3) that was subsequently explained by assuming that conjugation was an essential step prior to hydrogenation (21).

Unfortunately, under the conditions used in this investigation, triglycerides were not successfully conjugated without hydrolysis and ester exchange. Before this approach can be considered for practical applications, further work is required to develop a reagent or conditions to selectively conjugate the linolenyl group in soybean oil triglycerides.

ACKNOWLEDGMENTS

Mass spectral analysis was performed by Dr. W.K. Rohwedder, and heterogenized Cr carbonyls were prepared by R.A. Awl.

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[Received September 12, 1980]