Selective Hydrogenation of Soybean Oil: IV. Fatty Acid Isomers Formed With Copper Catalysts

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Abstract

Two samples of soybean oil hydrogenated with copper-containing catalysts at 170 and 200 C were analyzed for their natural and isomeric fatty acids. Methyl esters of the hydrogenated oils were separated into saturates, monoenes, dienes and trienes by countercurrent distribution between acetonitrile and pentane-hexane. Monoenes were further separated into *cis*- and *trans*-isomers on a silver-saturated resin column. Double bond location in these fractions was determined by a microozonolysis-pyrolysis technique. The diene fraction was separated with an argentation countercurrent distribution method, and linoleate was identified by infrared, ozonolysis and alkali-isomerization data. The double bonds in the *cis*-monoenes were located in the 9-position almost exclusively. However, the double bonds in the *trans*-monoene were quite scattered with 10- and 11-isomers predominating. About 86% to 92% of the dienes consisted of linoleate as measured by alkali isomerization. Other isomers identified as minor components include *cis,trans* and *trans, trans* conjugated dienes and dienes whose double bonds are separated by more than one methylene group.

Introduction

Hydrogenation of unsaturated esters in oils and fats with heterogeneous catalysts is invariably accompanied by geometric and positional isomerization of residual double bonds.

When polyunsaturated oils like soybean oil (SBO) are hydrogenated with commercial catalysts, a vast array of both positional and geometrical isomers is formed (6,10). Analysis and identification of these isomers are difficult because they have similar physical and chemical properties. With the advent of countercurrent distribution (CCD), column chromatography in the presence of silver ions and microozonization-pyrolysis techniques, it is now possible to separate and identify the various isomers that are formed during hydrogenation (6,9,10).

Since copper catalysts are much more selective than nickel (7) for the reduction of linolenate in SBO, there is considerable interest in copper catalysts for possible commercial use. No information, however, is available on their effect upon "natural" oleic and linoleic acids. The analysis of two soybean oils partially hydrogenated with copper catalysts is described in this report.

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Experimental Procedures

Materials

Two soybean oils, partially hydrogenated (IV 119–120) in a 2 liter Parr hydrogenator with laboratory-prepared catalysts containing copper (8) at 30 psi and 170 (sample A) and 200 C (sample B), respectively, were used in this investigation. Samples of each were transesterified in methanol with sodium methoxide catalyst, and the methyl esters were distilled under vacuum. Analyses of these esters are shown in Table I.

Analytical Methods

Fatty acid compositions were determined from gas chromatographic curves obtained with an 11% EGSS-X on Gas-Chrom P (Applied Science Laboratories, State College, Pa.) column and argon radium D ionization detector. Diene conjugation and per cent linolenate and linoleate were measured by the AOCS official spectrophotometric method (2). The percentage of isolated *trans* was estimated by infrared (IR) absorption of methyl esters in carbon disulfide with methyl elaidate as the standard.

Fractionation

Methyl esters (19–20 g) were separated into saturates, monoenes, dienes and trienes by CCD with an acetonitrile, pentane-hexane solvent system as described previously (12). Sample B fractions were combined as shown in Figure 1. The analytical data for the various fractions in both samples A and B are given in Table II. The diene fraction from sample A was further separated by CCD between 0.2 M $AgNO_3$ in 90% methanol and pentane-hexane solvent systems (11). Fractions were combined as illustrated in Figure 2. Table III contains the analytical data for the various fractions.

The monoene fractions from both samples were further separated into palmitate, *trans* monoenes and *cis* monoenes on a silver-saturated resin column (4).

Double Bond Location

Double bond position in the *cis* and *trans* monoenes was determined by the microozonolysis-pyrolysis procedure described by Davison and Dutton (3). The mole percent values of the different isomers based on the aldehyde ester fragments are plotted in Figure 3.

Results and Discussion

Analyses of esters from the two hydrogenated oils differed little. The oil hydrogenated at 200 C (sample B) had more conjugated dienes than that at 170 C

TABLE I

Analyses of Methyl Esters of Hydrogenated Soybean Oils

Hydrogenation sample	Fatty acid composition, % gas-liquid chromatography						*trans*, %	Ultraviolet conjugated diene, %	Alkali isomerization Le, %
	$C_{16:0}$[a]	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	CD			
A	10.0	4.2	35.9	47.1	1.8	1.0	7.5	0.8	0.7
B	10.3	4.1	34.8	47.0	2.0	1.9	8.1	3.5	0.7

[a] $C_{16:0}$ = palmitate; $C_{18:0}$ = stearate; $C_{18:1}$ = monoene; $C_{18:2}$ = diene; $C_{18:3}$ = triene + *cis,trans conjugated* diene; CD = *trans,trans* conjugated diene; Le = linolenate. Sample A = soybean oil partially hydrogenated at 170 C and 30 psi with a copper-chromite catalyst prepared by urea precipitation (8). Sample B = soybean oil partially hydrogenated at 200 C and 30 psi with a copper-chromite catalyst prepared by sodium borohydride reduction (8).

TABLE II
Analyses of Fractions from Countercurrent Distribution of Methyl Esters of Hydrogenated Soybean Oils

Fraction	Weight, %	Gas-liquid chromatography composition, %	*trans*, %	Ultraviolet conjugated diene, %
		Sample A		
Saturated	9.8	$C_{16:0}$ = 18.4; $C_{17:0}$(?) = 0.8; $C_{18:0}$ = 48.9; $C_{18:1}$ = 21.0; $C_{19:0}$(?) = 1.0; $C_{20:0}$(?) = 3.9; $C_{20:1}$(?) = 2.6; $C_{22:0}$(?) = 3.5	.....	....
Monoene	40.8	$C_{16:0}$ = 19.9; $C_{18:1}$ = 80.1	12.3	....
Monoene + diene	4.7	$C_{14:0}$ = 0.5; $C_{16:0}$ = 1.0; $C_{16:1}$(?) = 0.4; unknown = 0.3; $C_{18:1}$ = 34.8; $C_{18:2}$ = 60.7; *cis,trans* conjugated diene = 1.0; *trans,trans* conjugated diene = 1.3	.....	....
Diene	43.4	Diene = 97.5; *cis,trans* conjugated diene = 1.3; *trans,trans* conjugated diene = 1.2 (alkali isomerization, linoleate = 91.8%)	4.8	1.8
Triene	1.3	$C_{12:0}$ = 0.8; $C_{16:0}$ = 1.4; unknown = 1.0; $C_{18:1}$ = 2.6; $C_{18:2}$ = 13.2; $C_{18:3}$ = 74.2; conjugated diene-triene = 6.8 (alkali isomerization linolenate = 69.4%)	.....	....
		Sample B		
Saturated	8.5	$C_{16:0}$ = 14.7; $C_{17:0}$(?) = 1.4; $C_{18:0}$ = 55.7; $C_{18:1}$ = 16.8; $C_{19:0}$(?) = 1.1; $C_{20:0}$(?) = 4.2; $C_{20:1}$ = 2.3; $C_{22:0}$ = 3.8	.....	....
Monoene	38.0	$C_{16:0}$ = 23.0; $C_{18:1}$ = 77.0	18.0	....
Monoene + diene	5.9	$C_{14:0}$ = 0.6; $C_{16:0}$ = 3.4; $C_{16:1}$(?) = 0.2; unknown = 0.7; $C_{18:1}$ = 62.3; $C_{18:2}$ = 29.4; *cis,trans* conjugated diene = 1.1; *trans,trans* conjugated diene = 2.3	.....	....
Diene	46.4	Diene = 91.0; *cis,trans* conjugated diene = 4.4; *trans,trans* conjugated diene = 4.6 (alkali isomerization, linoleate = 86.6%)	5.3	6.7
Triene	1.3	$C_{12:0}$ = 0.5; $C_{16:0}$ = 0.3; unknown = 0.5; $C_{18:1}$ = 1.8; $C_{18:2}$ = 19.0; $C_{18:3}$ = 65.6; *trans,trans* conjugated diene = 0.9; conjugated diene-triene = 11.4 (alkali isomerization, linolenate = 61.5%)	.....	....

(sample A) (Table I). Even though both samples contained about 0.7% linolenate as measured by alkali isomerization, gas-liquid chromatography (GLC) indicated higher values. This difference was due to *cis,trans* conjugated dienes that elute along with trienes on GLC. In the isolated triene fractions (Table II), which are relatively free of interfering conjugated dienes, the GLC and alkali isomerization values were in reasonably good agreement.

Since CCD of the methyl esters (Table II) yielded only small amounts of triene, no further analyses were made except GLC and alkali isomerization. About 8% and 15% of the triene in samples A and B, respectively, had two double bonds in conjugation. Presumably the rest of the triene was linolenate. The diene fractions from both samples contained minor amounts (5%) of *trans* isomers. Ultraviolet analysis following alkali isomerization showed that 92% of the diene in sample A (87% in sample B) was linoleate. The diene from sample B contained more conjugation (6.7%) than the diene from sample A (1.8%). In both, the monoene fractions contained some palmitate, which was removed as a separate peak during silver-resin chromatography. Minor components of saturated fatty acids present in SBO were concentrated into saturate fractions. The identification of these acids was based only on the retention time on GLC and, hence, should be regarded as tentative. C_{17} and C_{19} saturated acids corresponded to less than 0.1% of the original SBO while the C_{20} and C_{22} acids comprised about 0.3%. C_{12} and C_{14} saturated acids, concentrated in triene and monoene-diene fractions, respectively, represented only trace amounts of the SBO.

The monoene fractions were further separated into palmitate, *trans* monoenes and *cis* monoenes. The

TABLE III
Analyses of Diene Fractions (Sample A)

Fraction	I	II	III	IV	V	VI	VII
Weight, %	3.3	3.1	26.4	33.5	19.9	11.8	1.9
trans, %	21.3	13.5		3.9		3.4	40.8
Ultraviolet conjugated diene, %	46.1	.....	.....	.....	.....	.....	.....
Alkali isomerization, linoleate, %	.....	92.3	99.8	97.4	96.7	92.3	7.2

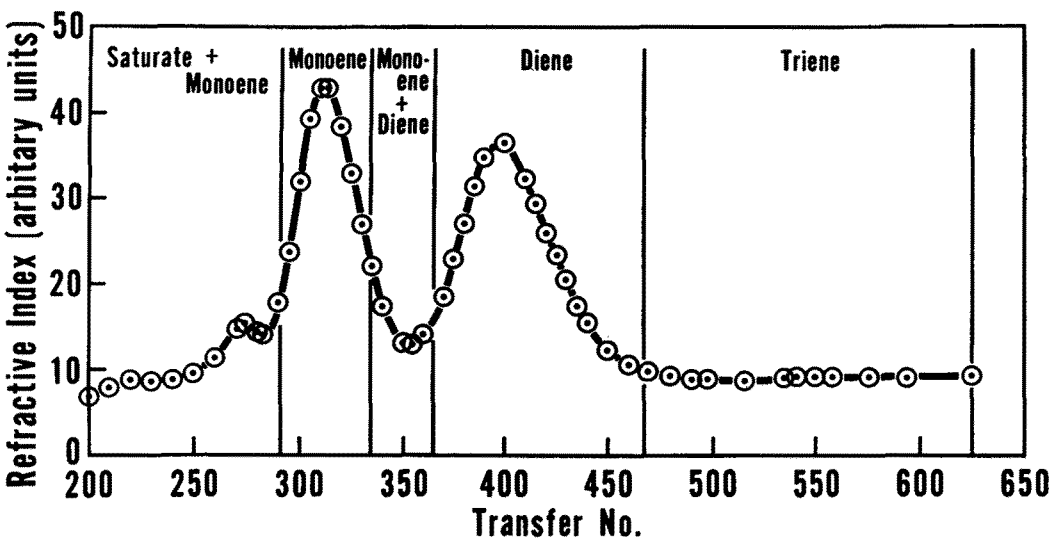

FIG. 1. Countercurrent distribution of hydrogenated soybean oil methyl esters (sample B) with acetonitrile and pentane-hexane.

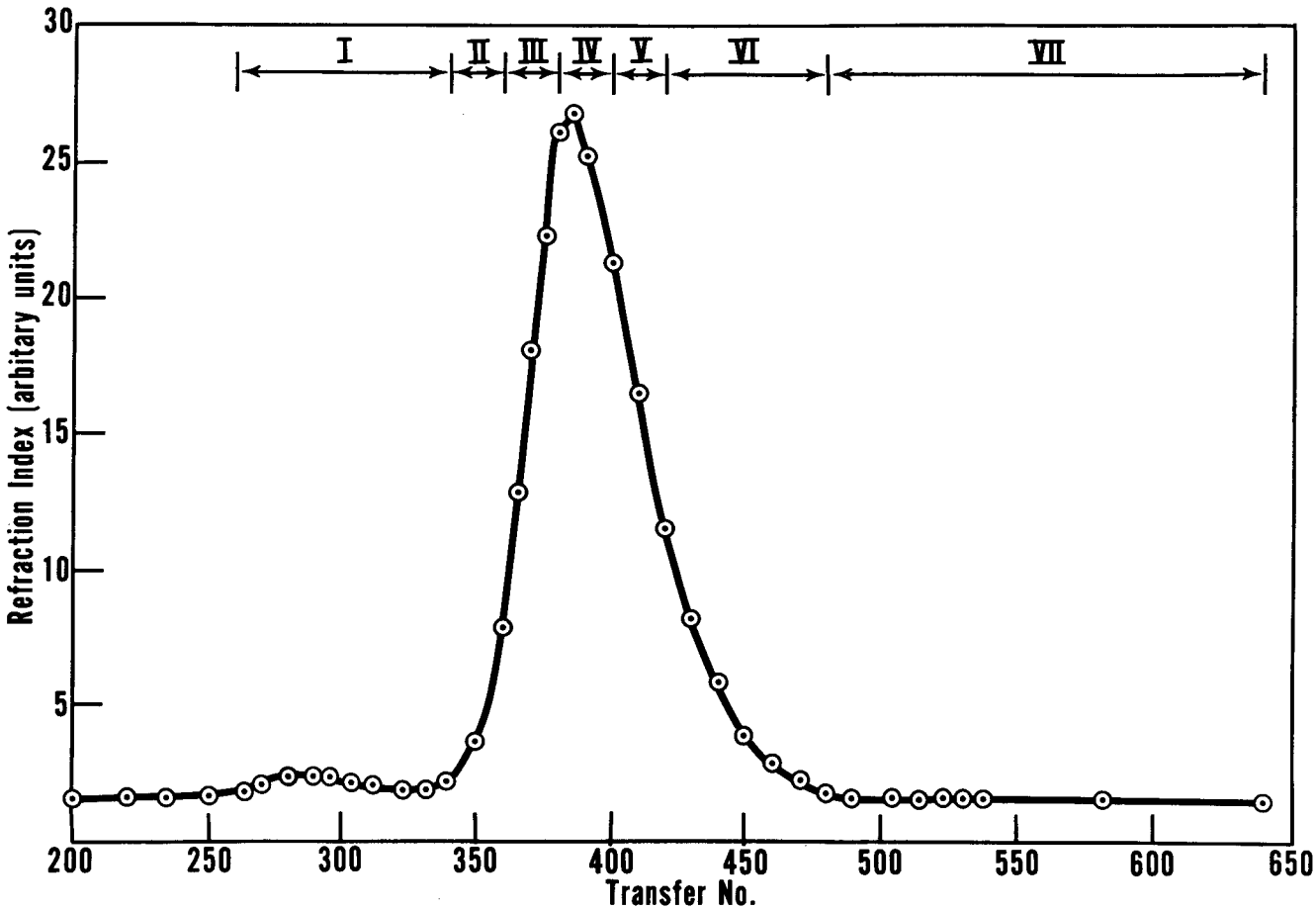

FIG. 2. Countercurrent distribution of dienes from sample A between 0.2 M $AgNO_3$ in 90% methanol and pentane-hexane.

double bonds in the *cis* monoene fraction were located almost exclusively in the 9-position. Apparently the original oleate in SBO remained unchanged during hydrogenation. Also, only minor amounts of *cis* monoenes were formed from the polyunsaturated fatty acids during partial hydrogenation. The double bonds in the *trans* monoene fractions (Fig. 3) were quite scattered with Δ^{10} and Δ^{11} isomers predominating. As expected, the *trans* monoene from sample B, which had been hydrogenated at the higher temperature, showed considerably more scattering of the double bonds. Therefore, since more of the objectionable conjugated dienes also were formed at the higher temperature, low-temperature hydrogenation is preferable

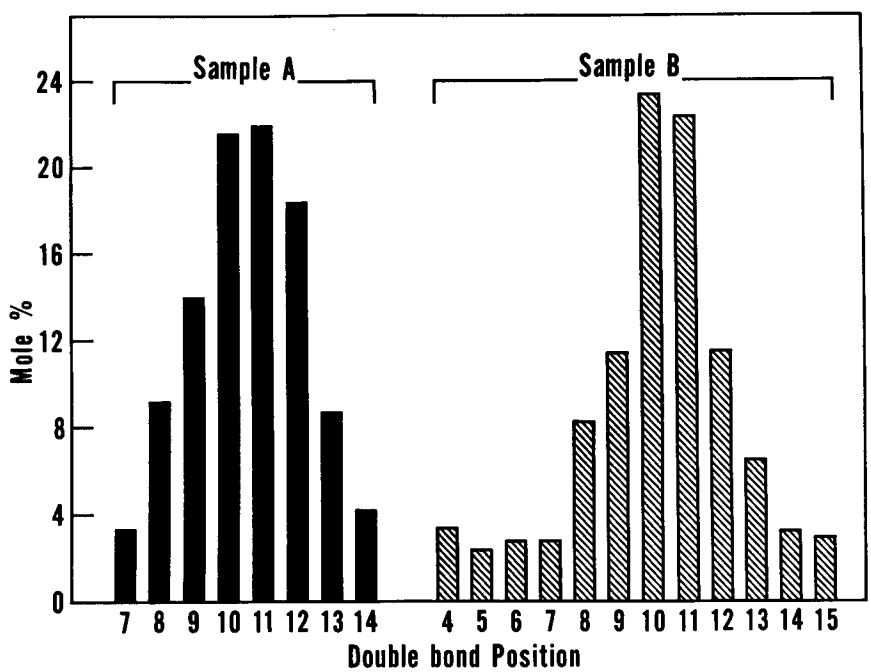

FIG. 3. Double bond distribution in *trans* monoenes.

TABLE IV

Calculated Composition of Two Hydrogenated Soybean Oils

Ester	Weight, %			
	Original SBO	Sample A	Original SBO	Sample B
Palmitate	10.0	10.0	10.3	10.3
Stearate	4.2	4.2	4.1	4.1
Oleate	26.0	30.4	22.7	26.7
trans-Monoenoate	...	5.5	.....	8.1
Linoleate	52.5	43.2	54.4	40.7
Conj. dienoate	.....	0.89	.....	3.5
Isolinoleate	....	5.2	.....	6.0
Linolenate	7.3	0.7	8.0	0.7

for the selective hydrogenation of SBO with copper catalysts, all other conditions being equal.

The diene fraction from sample A was fractionated by CCD with a silver nitrate system (Fig. 2), and the different fractions were analyzed (Table III). Fractions III, IV and V were combined because they were nearly pure linoleate as measured by alkali isomerization. IR analysis of the combined fraction showed only traces of *trans* isomers (3.9%). Oxidative ozonolysis (1) followed by GLC analysis of the mono- and dicarboxylic acids as their methyl esters showed that the double bonds were located at the 9- and 12-positions. Apparently this combined fraction consisted essentially of linoleate. Fraction I, which comprised 3.3% of the diene, was composed chiefly of conjugated dienes. Fraction VII, which amounted to 1.9% of the diene, contained 40.8% *trans* and little alkali isomerizable diene (7.2%). Nuclear magnetic resonance analysis (5) indicated that 56.5% of the molecules had unsaturation at the 15–16 bond. Therefore, this fraction largely consisted of diene in which the double bonds are separated by more than one methylene group. From the analysis of all fractions, the approximate composition of the hydrogenated SBO methyl esters was calculated. The composition of the original SBO and the calculated composition for the hydrogenated oil are shown in Table IV.

The composition of hydrogenated oil was calculated as follows: Because there is no increase in saturates, they are present in the same amounts as in the original SBO esters. The monoene fraction from CCD analyzed 15.4% *trans* when corrected for palmitate (sample A, Table II). Sample A contained 35.9% monoene; therefore, the amount of *trans* monoene in sample A is $35.9 \times 0.154 = 5.5\%$. The remaining monoene is oleate since double bonds are located in the 9-position for the *cis* monoene fraction. Conjugated dienes were established by ultraviolet analysis (Table I). Also, 91.8% of the diene is linoleate as measured by alkali isomerization (sample A, Table II). Sample A contains 47.1% diene; therefore, $47.1 \times 0.918 = 43.2\%$ is linoleate. Alkali isomerization showed 0.7% linolenate. The remaining polyunsaturated acid ester is assumed to be isolinoleate.

A comparison of the copper hydrogenated SBO from this work with nickel hydrogenated liquid oils (6,10) indicates that the esters formed during hydrogenation are similar. However, because of the superior selectivity of copper catalysts, the linolenate content of SBO can be reduced to less than 1% with formation of only about 8% *trans* isomers. On the other hand, nickel hydrogenated SBO contained 2–4% linolenate and considerably more *trans* isomers (12–15%). Copper catalysts have the added advantage of minimizing reduction of the desired linoleate.

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