Hydrogenation of Soybean Oil Triglycerides: Effect of Pressure on Selectivity[1]

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ABSTRACT: Soybean oil contains five triglycerides that account for over 70% of the total. These include LLL, LLO, LLP, LOO, and LOP and their isomers (where L = linoleic, O = oleic, P = palmitic). High-performance liquid chromatographic analysis of samples taken during a typical hydrogenation run in which the iodine value (IV) was reduced from 130 to about 70 showed that the linoleate-containing triglycerides were reduced at a much faster rate than the linolenate-containing triglycerides. Results clearly show that hydrogenation proceeds through definite pathways rather than by random saturation of fatty acids within the triglyceride molecules. Pressure has a significant effect on the course of hydrogenation. At higher pressures (500 psi), the reaction is truly nonselective, since di- and trisaturated glycerides are formed at about 70 IV, whereas at 50 psi, the reaction becomes selective. At higher pressures, fat functionality and solid fat result primarily from di- and trisaturated fatty acid triglycerides as well as *trans* fatty acid triglycerides. At lower pressures, functionality results from *trans* acid triglyceride formation. Although the reactivity of linoleate containing triglycerides followed the pattern 6 double bonds > 5 double bonds > 4 double bonds, other factors may be important. For example, LLP is reactive and undergoes hydrogenation, while LLS remains unchanged. Triolein, which constitutes less than 3% of the total triglyceride in natural soybean oil, is a significant product of hydrogenation, which suggests that LLL and LLO are reduced directly while adsorbed on the catalyst surface.

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The theory of edible oil hydrogenation was outlined in a series of papers by A.E. Bailey (1,2) and expanded by Dutton (3), Allen (4), and Albright (5). A recent review pointed out that, despite much research, a number of questions remain unsolved, including positional, *trans* fatty acid, and triglyceride selectivity (6). Virtually every previous kinetic, mechanistic, and isomerization study has employed analyses of methyl esters rather than the intact triglycerides. We report here studies made on the analysis and separation of hydrogenated soybean oil triglycerides by high-performance liquid chromatography (HPLC).

EXPERIMENTAL PROCEDURES

The soybean oil used in this study was a commercially refined, bleached, and deodorized salad oil obtained from Riceland Foods (Stuttgart, AR). A commercially prepared 25% nickel-supported catalyst was used, and the final nickel content used for hydrogenation was 0.02% by weight oil. Hydrogenations were carried out in a 2-L stirred reaction vessel (rated for 5,000 psi pressure). Hydrogenation reactions were conducted under conditions known to be nonselective: 120°C, 50–500 psi, and high stirring (1). Iodine value (IV) drops were monitored by changes in refractive index.

HPLC. Reversed-phase (RP)-HPLC was performed with a Thermo Separation Products (model SP 8800; Schaumberg, IL) ternary solvent system with two RP-HPLC columns with bonded silyl (CT8) ODS, Inertsil ODS-80A (GL Sciences, Keystone Scientific, Bellfonte Park, PA), 25 cm × 4.6 mm, 5 μm in series. The gradient elution was as follows: 80% acetonitrile (ACN), 20% dichloromethane (DCM) to 20% ACN, 80% DCM after 120 min. The flow rate was 0.6 mL/min throughout. Sample size (25 μg) injected was 10 μL of 25 mg solute/mL DCM.

*Evaporative light-scattering detector (ELSD).*The ELSD was a Sedex model 55, Sedone (Altonville, France). The drift tube was set at 32°C. The gas flow was set at a pressure of 1.6 bar. The photomultiplier gain was times five. High-purity N_2 was used as the nebulizer gas.

Triacylglycerol identification. The triacylglycerol HPLC chromatogram peaks were identified based on earlier analysis of soybean oil *via* RP-HPLC coupled with an atmospheric pressure chemical ionization mass spectrometer (7,8).

Data processing. The data output from ELSD was processed or integrated by a Star Chromatography Workstation with version 4.0 software, Varian Associates, Inc. (Walnut Creek, CA).

Gas chromatography (GC). Fatty acid methyl esters (FAME) were prepared by the potassium hydroxide-catalyzed transmethylation of the triacylglycerol mixtures, and the FAME were analyzed using calibrated GC according to a previous procedure (9).

RESULTS AND DISCUSSION

Fatty acid compositional data for the hydrogenated oils along with IV and *trans* isomer content are given in Table 1. The

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TABLE 1
Fatty Acid Composition of Soybean Oils Hydrogenated Under Nonselective Conditions

				Fatty acid (%)[a]							Iodine value		
Oil	Temp (°C)	H_2 pressure (psi)	Time (h)	C16:0	C18:0	C18:1(*c*)	C18:1(*t*)	C18:2(*c*)	C18:2(*t*)	C18:3	Ref. index	GLC esters[b]	GLC TG[c]
Unhydrogenated			0	11.9	4.4	23.9	0.0	54.4	0.0	5.4	129	128.9	132.8
Hydrogenated	120	50	1	10.9	4.5	25.8	1.2	49.3	1.5	4.5	124	123.0	128.3
Hydrogenated	120	50	2	11.0	5.8	36.1	6.5	33.2	3.5	2.1	105	105.7	107
Hydrogenated	120	50	3	11.1	8.7	46.3	13.4	14.8	4.4	0.5	86	85.9	81
Hydrogenated	120	50	4	11.7	16.8	39.4	22.0	5.3	4.1	0.0	69	69.1	65.2
Hydrogenated	120	500	1.3	10.7	7.6	25.5	1.8	46.5	1.5	4.3	118	117.9	121.5
Hydrogenated	120	500	2	10.8	11.0	26.5	3.2	41.3	1.7	3.7	110	109.7	118.1
Hydrogenated	120	500	3	10.9	18.0	27.3	5.5	32.2	1.9	2.7	94	94.3	100.6
Hydrogenated	120	500	4	10.7	26.9	27.5	8.2	21.8	2.2	1.6	76	76.5	83.7

[a] *c = cis, t = trans.*
[b] Calculated from composition of esters by gas–liquid chromatography (GLC).
[c] Calculated from composition of triglycerides (TG) by GLC.

data clearly show that, under the conditions employed, the reactions appear nonselective because stearic acid increases as hydrogenation progresses. However, examination of the triglyceride patterns shows an entirely different picture, as shown in Figure 1. The top portion shows the triglyceride distribution from the 500 psi run, whereas the bottom half represents the 50 psi pressure. Hydrogenated soybean triglycerides contain five major components that represent about 70% of the total. They include LLL, LLO, LLP, LOO, and LOP (where L = linoleic, O = oleic, S = stearic, P = palmitic) at concentrations of about 19.0, 19.0, 13.8, 8.8, and 9.4%, respectively. At 500 psi, these five triglycerides follow the kinetic pattern:

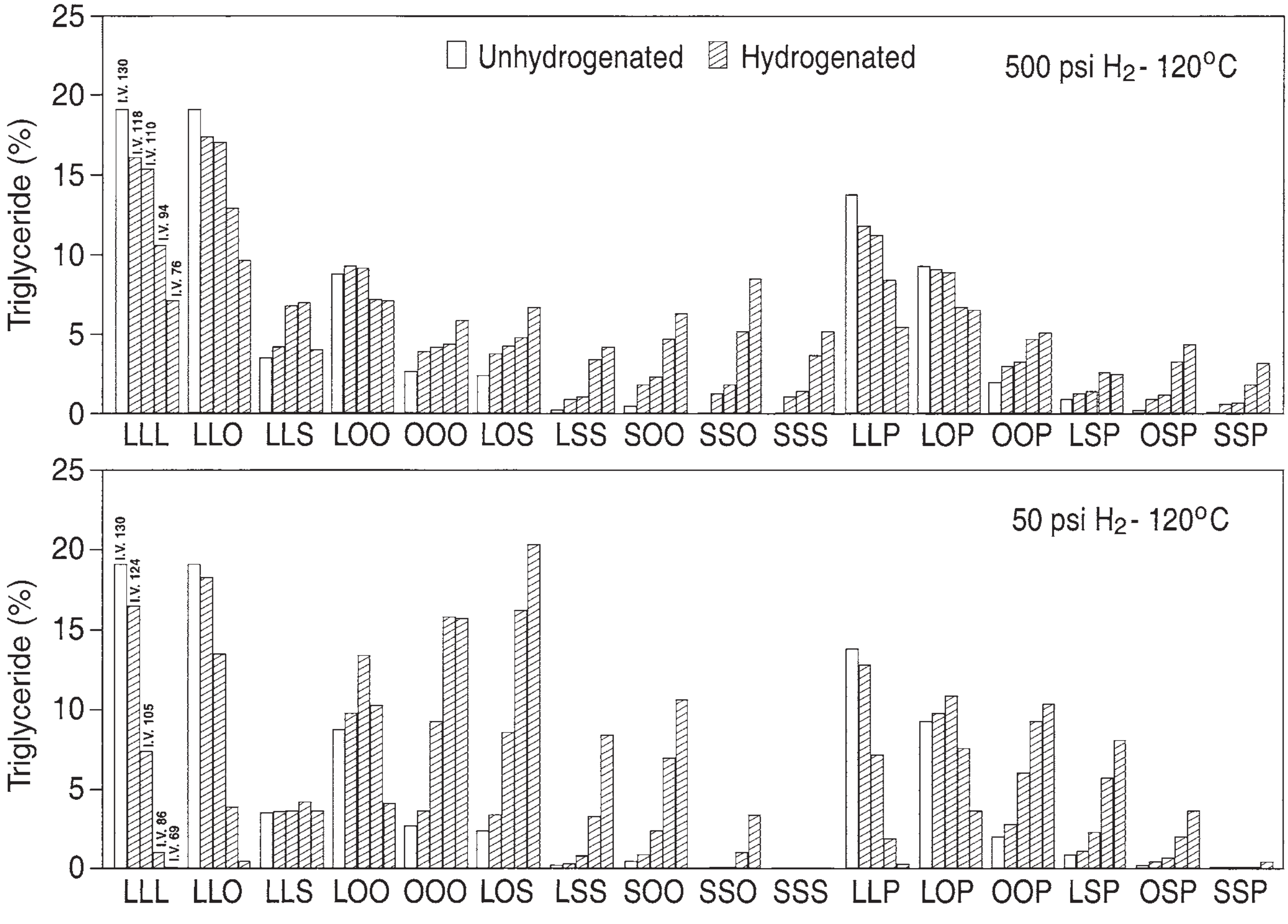

FIG. 1. Effect of hydrogenation pressure on linoleate-containing triglycerides in soybean oil. L, linoleic; O, oleic; P, palmitic; S, stearic acid. I.V., iodine value.

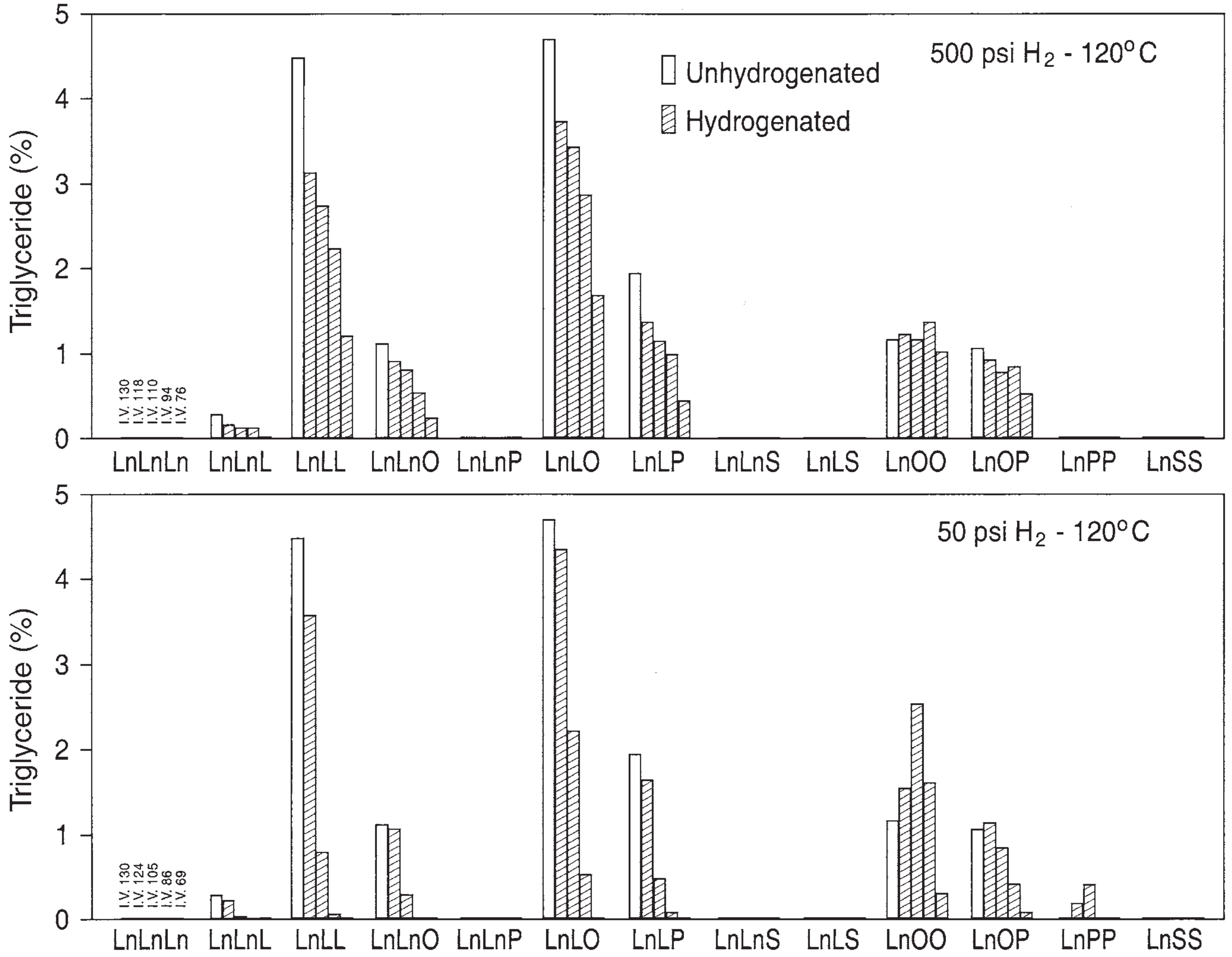

FIG. 2. Effect of pressure and time of hydrogenation on linolenate-containing triglycerides in soybean oil. Ln, linolenic acid; for other abbreviations see Figure 1.

LLL → OOO → OOS → OSS → SSS
LLO → OOO → OOS → OSS → SSS
LLP → OOP → OSP → SSP
LOO → OOO → OOS → OSS → SSS
LOP → OOP → OSP → SSP

At 50 psi the kinetic pattern can be represented as follows:

LLL → OOO → OOS → OSS
LLO → LOS → LSS
LLP → OOP → OSP

The effects of hydrogenation on the linolenic acid-containing triglycerides (LnLL, LnLO, and LnLP) are shown in Figure 2. Under the conditions of hydrogenation favoring low selectivity, these triglycerides are reduced slowly. Possible kinetic schemes include LnLL being reduced to LLL, LnLO being reduced to LLO, and LnLP being reduced to LLP, which, in turn, are reduced according to schemes discussed above. Thus, at 500 psi pressures the hydrogenations are truly nonselective since trisaturated triglycerides are formed, whereas, at 50 psi, trisaturated triglycerides are absent. Other data (not shown) indicate that the pressure region where trisaturated triglycerides are formed is fairly narrow since data gathered at 100 psi appear much like the 500 psi pressure data. Thus, between 50–100 psi, the course of hydrogenation is changed from selective to nonselective. Other data indicate that modest increases in temperature can be used to further control the reaction such that products with different properties, such as solid fat index (SFI), dropping points, and *trans* content can be made. For example, products made at 120°C and 100 psi pressure have high SFI profiles more suited to shortenings, whereas at 50 psi, higher, steeper profiles result in making the products more amenable to margarines/spreads.

Although the high performance chromatography method employed here will not distinguish between positional isomers, the five major triglycerides in unhydrogenated soybean oil are most certainly correctly identified (7,8), since saturated acids are absent from the 2-position in naturally occurring oil. An exception would be LLO, which would include smaller amounts of LOL. Close agreement between IV obtained from direct analysis vs. the theoretical IV calculated from the individual triglycerides indicates the method gives reliable data and should prove useful for quality control purposes. Some loss of resolution, however, was noted in some heavily hydrogenated samples.

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