High Oleic Oils by Selective Hydrogenation of Soybean Oil[1]

OVIDIU POPESCU,[2] SAMBASIVARAO KORITALA and H. J. DUTTON,
Northern Regional Research Laboratory,[3] Peoria, Illinois 61604

Abstract

High oleic (monoene) oils were obtained from soybean oil by selective hydrogenation with copper catalysts. A mixture of nickel and copper chromite catalyst had activity suitable for producing the high monoene oils. A new catalyst (copper-on-Cab-O-Sil) prepared in the Laboratory was more active than commercial copper catalysts. Hydrogenated oils contained 61–72% monoenoic and 14–24% dienoic acids, and there was essentially no increase in stearic acid. The *trans*-isomer content of these oils varied between 17% to 32%. Double bonds in the monoene were distributed along the molecule from C_6 to C_{15}, but were located preferentially in the C_9 position for the *cis*-monoene and in the C_{10} and C_{11} positions for the *trans*-monoene. When the iodine value of these high monoene oils was about 90–95, they remained liquid above 28 C. Citric acid treatment reduced the copper content of hydrogenated oils to a level that was comparable to that of the original soybean oil.

Introduction

Copper-chromite catalysts possess high selectivity for linolenate over linoleate and an infinite selectivity towards linoleate over oleate (7). Hydrogenation of polyunsaturated oils with these catalysts stops at the monoene stage. Therefore, oils with a high monoene (oleic) content should be readily prepared from soybean oil (SBO) by selective hydrogenation with copper catalysts. Some preliminary findings are reported here on the hydrogenation of SBO at low and high temperatures and at low and high pressures. Hydrogenation experiments with a catalyst mixture of nickel and copper chromite are included, as well as a two-step hydrogenation, nickel followed by copper.

Experimental Procedures

Apparatus

Two different hydrogenators were used in the production of high monoene oils: a Parr hydrogenator with a modified stirrer as described by Beal and Lancaster (2), and a 3 gal stainless steel convertor, provided with electric thermostated heating and with cooling coils.

Analytical Methods

Methyl esters were prepared from triglycerides by transesterification with 0.5% sodium methoxide catalyst and their compositions were determined by GLC. A Pye chromatograph, equipped with a 4 ft × ¼ in. glass column packed with 11% EGSS-X on Gas-Chrom P, 100–120 mesh (organosilicon polyester packing from Applied Science Laboratories, Inc., State College, Pa.) and with a radium D ionization detector, was operated at 170 C with an argon gas flow of 45 ml/min. The area under each peak was determined from an electronically integrated curve.

Contents of conjugated dienoates, linolenate and linoleate were estimated by the AOCS Official Method (1) with a Cary Model 14 recording spectrophotometer. *Trans*-isomers were estimated with a Perkin-Elmer 621 infrared spectrophotometer by comparing the absorption at 10.36 μ to that of methyl elaidate.

Methyl esters of selected hydrogenated products were separated into saturates, monoenes and dienes on a rubber column (5). Monoenes were further separated into *cis*- and *trans*-fractions by chromatography on a silver-saturated cation exchange resin (4). The position of the double bonds in *cis*- and *trans*-isomers was determined with microreactor gas chromatography (3).

Hydrogenation

Soybean oil (1 liter for a Parr apparatus; 3 to 5.7 liters for a 3 gal convertor) and the catalyst were charged into the hydrogenator, purged with hydrogen gas, and then heated under vacuum with stirring. At 20 degrees below the hydrogenation temperature, stirring was stopped and hydrogen was introduced. When the proper temperature was attained, stirring was restarted and the progress of hydrogenation was measured by the drop in hydrogen pressure in an external reservoir. The drop in iodine value was calculated from the amount of hydrogen uptake. When the required amount of hydrogen was reacted, hydrogenation was stopped by evacuating the gas and cooling the oil under vacuum. The conditions of hydrogenation, the catalysts and the amounts used, as well as the type of apparatus, are shown in Table I.

Discussion of Results

Activity of Catalysts

Activities of the catalysts were evaluated by the drop in iodine value versus time (Fig. 1). Initially, commercial catalysts showed high activity (Exp. 1

TABLE I
Conditions of Hydrogenation of Soybean Oil

Experiment no.	Catalyst		Temp., C	Pressure, psi	Time, min	Type of apparatus
	Source	%, w/v				
1	Cu-1106P[a]	1.0	170–175	30	300	Parr
2	G-22[b]	0.5	200–220	30	270	Parr
3	Cu-1106P	1.0	180	400–100	318	3 Gal
4	G-49A[c]	0.14	170–205	15	12	3 Gal
5	Cu-1106P	1.0	220	55–30	350	3 Gal
6	G-49A+ Cu-1106P	0.03+ 1.0	180–238	55–25	35	3 Gal
7	10% Copper on Cab-O-Sil[d]	1.0	170–195	55–35	37	3 Gal

[a] Commercial copper-chromite catalyst (CuO, 39%; Cr_2O_3, 43.5%; BaO, 10%).
[b] Commercial copper-chromite catalyst (CuO, 42%; Cr_2O_3, 40%; BaO, 12%).
[c] Commercial nickel catalyst reduced and stabilized (65% Ni).
[d] Reference 6.

---

[1] Presented at the AOCS Meeting, Chicago, October 1967.

[2] Food and Agricultural Organization representative from Rumania. Present address: Bd. Schitul Maghreanu 39, Bucharest, Rumania.

[3] No. Utiliz. Res. Dev. Div., ARS, USDA.

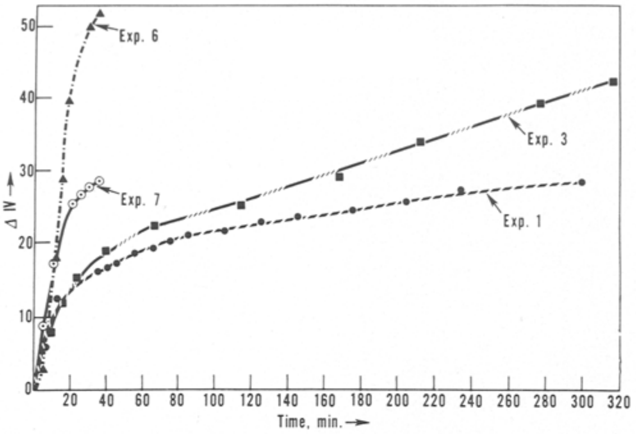

FIG. 1. Activity of catalysts in terms of hydrogen absorption (ΔIV) vs. time. Experiments as listed in Table I.

and 3), but after 30 min (almost all the linolenate was hydrogenated at this point) the activity quickly diminished. A mixture of nickel and copper chromite had good activity (Exp. 6).

In the two-step process, SBO was first hydrogenated with a nickel catalyst to reduce some of the polyunsaturates without increasing the saturates (Exp. 4). This oil was then hydrogenated with copper chromite (Exp. 5). It was hoped that the high initial activity of the copper catalysts would be saved for the final selective hydrogenation of polyunsaturated acids to monoenes; however, the time required to reduce the oil was too long to be practical. A laboratory-prepared catalyst (6) showed much greater activity than commercial catalysts even though much less copper was used (Exp. 7).

Composition of Hydrogenated Oils and Selectivity

The fatty ester composition and other analytical data for hydrogenated products are given in Table II. It is evident from the fatty ester composition (except in the final sample in Exp. 6 where hydrogenation was carried too far) that stearate increases only slightly. The monoenoate content reached values of 60% to 72% in Experiments 2, 3, 5 and 6.

Since these hydrogenations produced high-monoene oils, the catalysts and some of the techniques used for producing them may be of industrial interest. The high-monoene oils in Table II (Exp. 2, 3, 5 and the first sample in 6) are liquid at 28 C; but at room temperature (25 C) some solids separate from the liquids. The *trans*-isomer content in these oils varied between 22% and 32%. At an iodine value of 90–95 (decrease in iodine value of 40–45 units) the content of monoenoate is about 61–66% and of dienoate about 20–24%.

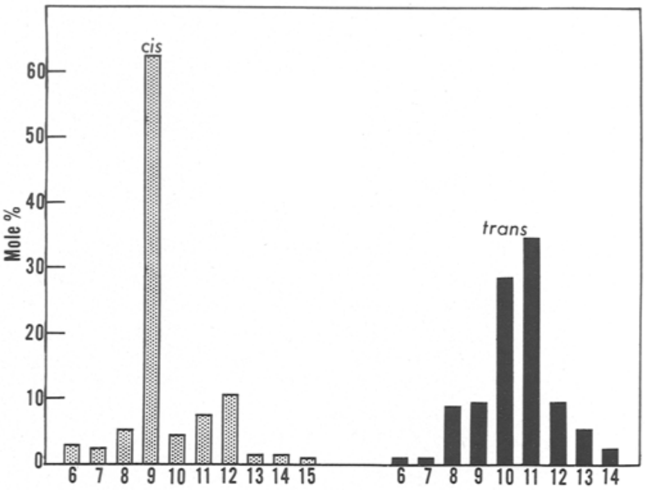

FIG. 2. Double bond distribution in *cis*- and *trans*-monoene fractions (Exp. 3).

Double Bond Distribution

Because the main components in high-oleic oils are monoenoic acids, the location of the double bonds in these fatty acids is significant. The double bond location in *cis*- and *trans*-monoenes from two samples is shown in Figures 2 and 3. More than 55% of the double bonds are located in the 9-position for the *cis*-monoenes. The remaining 45% appear along the chain from 6- to 15-positions. In the *trans*-monoene fractions the double bonds are more widely scattered, with the 10- and 11-positions predominating.

The mole per cent of monoenoic acid (*cis* plus *trans*) versus double bond position in the molecule is plotted in Figure 4. These values were calculated from the composition of the various *cis*- and *trans*-isomers and from the *trans* content of the monoene fraction. The monoene fractions of the two high-monoene oils analyzed contained about 37–39% of their double bonds in the 9-position, about 14% in the 10-position, 13–18% in the 11-position and 10–11% in the 12-position. The percentage of true oleic (*cis*-9-octadecenoic) acid in the monoene fractions is about 36–38% or about 25% of the high-monoene oils. The original SBO contained 25% oleate. Apparently very little, if any, true oleate is formed during hydrogenation of polyunsaturated esters of SBO.

Removal of Copper

One of the disadvantages encountered with copper hydrogenations is the contamination of oils; copper is a strong prooxidant. An attempt was made, therefore, to remove the copper from the high-monoene oils. The following methods were investigated: (a) Heating the oil to 75 C under nitrogen, adding 0.3%

TABLE II

Analytical Results of Hydrogenated Soybean Oil

Experiment no.	% Fatty ester GLC				Iodine value calc.	Alkali isomerization			
	St[a]	M[a]	D[a]	T[a]		% Lo[a]	% Le[a]	% Conj. dienes	% *trans*
Original soybean oil for Exp. 1 and 2	4	25	53	10	136	50.2	8.3	....	......
Original soybean oil for Exps. 3 to 7	4	25	52	9	136	45.5	7.5	....	......
1	4	48	38	1	108	28.1	0.0	0.6	18.9
2	4	61	24	0	94	......	....	....	29.6
3	5	63	23	0	94	10.0	0.0	0.0	32.3
4	5	48	36	3	110	23.1	2.2	0.0	21.7
5	5	72	14	0	83	5.6	0.0	....	31.6
6	5	66	20	...	91	11.1	0.2	0.0	27.1
	16	73	2	0	66	....	....	....	42.6
7	4	51	36	0	106	28.0	0.0	0.0	19.5

[a] St, stearate; M, monoenoate; D, dienoate; T, trienoate; Lo, linoleate; Le, linolenate.

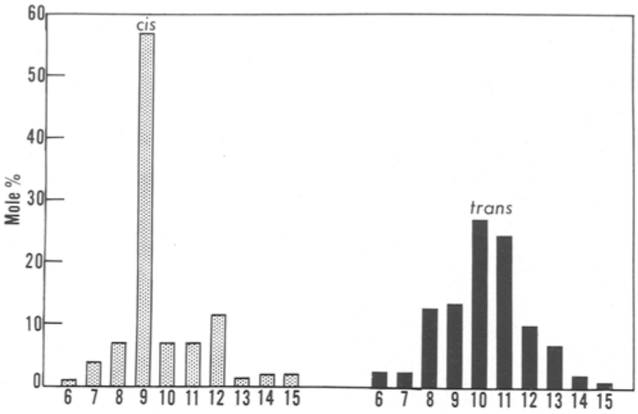

FIG. 3. Double bond distribution in *cis*- and *trans*-monoene fractions (Exp. 5).

of a 33% citric acid solution, stirring for ½ hr, applying vacuum at about 110–115 C to remove the moisture and, finally, filtering the cooled oil under vacuum over Celite; (b) the same procedure as under (a) except 0.2% concentrated phosphoric acid was used instead of citric acid; and (c) refining the oil with sufficient 10% NaOH solution that corresponded to 20% in excess of the theoretical amount required to neutralize the free fatty acids. The results given in Table III show that copper contaminant can be readily removed from the hydrogenated products either by a citric or phosphoric acid treatment or by a refining process.

TABLE III

Copper Content of Oils

Sample	Copper, ppm[a]
Original soybean oil	0.04
Original soybean oil	0.03
Experiment 5	1.63
Experiment 3	0.44
Experiment 3 (citric acid treatment)	0.02
Experiment 3 (phosphoric acid treatment)	0.02
Experiment 3 (alkali refining)	0.04

[a] Copper analyses made by an industrial laboratory with atomic absorption spectrophotometry.

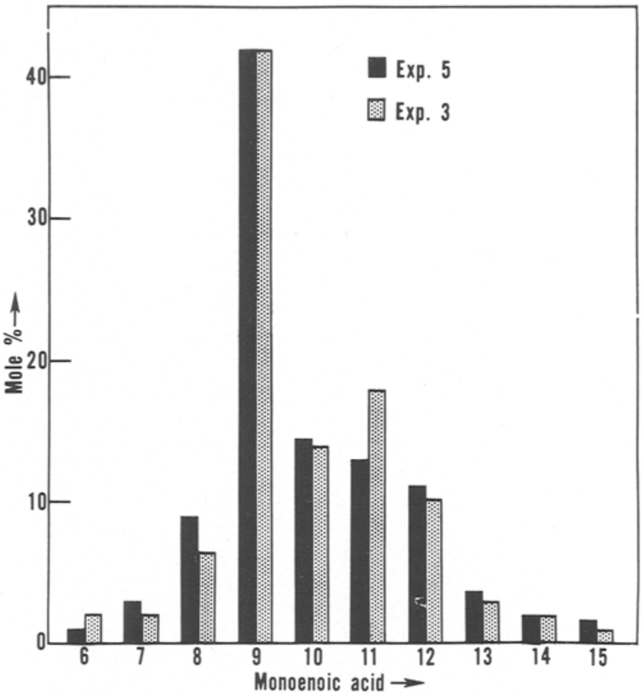

FIG. 4. Double bond distribution in monoenes.

ACKNOWLEDGMENTS

Infrared analyses by R. L. Hoffmann; microreactor gas chromatographic analyses by V. L. Davison; and rubber-column and silver-saturated cation exchange column chromatography by C. R. Schofield.

REFERENCES

1. AOCS Official and Tentative Methods, 2nd Ed., Cd 7–58, Revised to 1962, Chicago, Illinois.
2. Beal, R. E., and E. B. Lancaster, JAOCS *31*, 619–625 (1953).
3. Davison, V. L., and H. J. Dutton, Anal. Chem. *38*, 1302–1305 (1966).
4. Emken, E. A., C. R. Scholfield and H. J. Dutton, JAOCS *41*, 388–390 (1964).
5. Hirsch, J., Colloq. Int. Centre Nat. Rech. Sci. (Paris) *99*, 11 (1961).
6. Koritala, S., JAOCS *45*, 197–200 (1968).
7. Koritala, S., and H. J. Dutton, Ibid. *43*, 556–558 (1966).

[Received September 23, 1968]