Conversion of Polyunsaturates in Vegetable Oils to *Cis*-Monounsaturates by Homogeneous Hydrogenation Catalyzed With Chromium Carbonyls[1]

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Abstract

Chromium carbonyl complex catalysts were used to selectively hydrogenate polyunsaturates in vegetable oils into products retaining 90% to 95% *cis* configuration and their liquid properties. The product from soybean oil contained 42–69% monoene, 10–40% diene and 0–4% triene. The product from safflower oil contained 73–82% monoene and 8–17% diene. About 45–55% of the double bonds in monoenes from hydrogenated soybean oil remained in the C_9 position, and the rest was distributed between C_{10}, C_{11}, and C_{12}. Preliminary oxidative and flavor stability evaluations showed that these hydrogenated soybean oils compared favorably with a commercial sample of hydrogenated-winterized soybean oil. Liquid fatty acids prepared by saponification of hydrogenated soybean and safflower oils (IV 90–100) had analyses about the same as those of commercial oleic acid.

Introduction

Much work has been done on the partial hydrogenation of vegetable oils with various catalysts to improve the oxidative stability of salad or cooking oils. The selective hydrogenation of polyunsaturated fatty acid components of vegetable oils has been difficult to achieve without also producing geometric (*cis, trans*) and positional isomerization of double bonds (1). Generally to obtain liquid salad oils it is necessary to winterize the hydrogenated oils to reduce the level of high-melting *trans* and saturated products (2,3).

In a previous study of the homogeneous hydrogenation catalyzed by group VIB metal carbonyl complexes (4), we found that the $Cr(CO)_3$ complexes are selective in reducing polyunsaturated fatty esters without forming saturates. Of particular importance was our finding that the hydrogenated products were predominantly *cis* in configuration. This work has now been extended to the hydrogenation of soybean and safflower oils to prepare liquid oils high in *cis* unsaturation and liquid *cis* monoene fatty acids which have about the same analyses as commercial oleic acid.

Experimental Procedures

Materials and Methods

The vegetable oils used and methods of analysis (GLC, IR, UV, and alkali conjugation) were the same as those already described (5,6). Procedures for separation of monoene fractions and determination of double bond positions were cited previously (4). Determinations of fatty acids (free fatty acids and saponification values), AOM stability and cloud points were by standard AOCS procedures. Chromium trace analyses were made by atomic absorption spectrophotometry (Evans, unpublished data).

Hydrogenation

Most runs were made in a 150 ml, 300 ml, or 1 liter Magne-Dash stainless-steel autoclave, with or without solvent (cyclohexane). Large-scale runs (1 liter) were made in a 2-liter rocker-shaker autoclave. The scale of the run and size of the autoclave had generally little or no effect on the rate and extent of hydrogenation with the soluble catalysts used in this work. In run 4, for example (Table I), 200 ml of soybean oil (188 g) was charged into a 300 ml autoclave with 2.1 g methyl benzoate-$Cr(CO)_3$. The sealed autoclave was purged three times with hydrogen (500 psi) and then pressurized to 320 psi. The reaction mixture was heated to 175 C in 40 min. The pressure was then adjusted from 350 to 500 psi and hydrogenation continued for 4 hr. Samples were taken for analyses and pressure was restored to 500 psi every 0.5–1 hr. The hydrogenated product was water-cooled to room temperature. IR analysis (4) showed that it contained intact catalyst by the intense carbonyl bands at 1985 and 1915 cm^{-1}. The presence of decomposed catalyst was also indicated by the green color of the product.

The methyl benzoate-$Cr(CO)_3$ catalyst was removed by vacuum stripping for 2 hr at 160–185 C/0.3–0.5 mm in a rotating evaporator. Since the amount of catalyst recovered by this procedure varied, no attempt was made to determine yields. However, the benzoate-$Cr(CO)_3$ complex collected on the dry-ice trap was crystalline and as active as the original catalyst. An alternative procedure to remove $Cr(CO)_3$ catalyst was to decompose it with a mild oxidizing agent such as $FeCl_3$ under nitrogen (4).

Even though the stripped oil was free of catalyst as shown by the absence of carbonyl bands in the IR, it still remained green in color. The hydrogenated oil was then filtered through fritted glass (medium pore) to remove suspended and decomposed catalyst. The oil was then bleached by treating it with 10% (w/w) carbon black (Darco G-60) and stirring with N_2 bubbling on a steam bath 15 min. The cooled oil was clear after filtering again through fritted glass. Alternatively, the green, decomposed catalyst complex was removed by stirring with H_3PO_4 (1.2% w/w) for 45 min with N_2 bubbling and then removing the acid from a petroleum ether solution by repeated washing with water until neutral. The bleached oil was then deodorized at 210 C/0.4 mm for 2 hr.

Saponification

Fatty acids were prepared from hydrogenated oils by a standard saponification procedure (10 g scale) with KOH in 95% ethanol. Distillation of the ex-

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TABLE I

Hydrogenation of Vegetable Oils Catalyzed by Arene-$Cr(CO)_3$ Complexes[a]

Reaction parameters and analyses	Control	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Control	Run 9	Run 10
Oils	SBO	SBO	SBO	SBO	SBO	SBO	SBO	SBO	SBO	SFO	SFO	SFO
Conditions[b]												
Catalyst (arene)	....	Benzoate	Benzoate	Benzoate	Benzoate	Benzoate	Benzoate	Benzene	Benzene	....	Benzoate	Benzoate
Catalyst conc. M%	....	2	2	2	2	2.5	5	2.5	5	....	2	4
Solvent	....	None	None	None	None	Cyclo	Cyclo	Cyclo	Cyclo	....	None	None
Temp., C	....	145	155	165	175	165	165	175	175	....	175	175
Time, hr	....	4	4	4	4	6	6	6	6	....	1.5	2
Analyses												
GLC[c]												
Palmitate, %	10.3	10.3	10.1	10.3	10.4	10.3	10.2	10.5	10.5	7.3	6.7	7.0
Stearate, %	4.1	3.9	4.1	4.3	3.6	4.2	4.1	4.4	4.0	2.9	2.9	2.9
Monoene, %	23.1	42.0	51.9	60.7	63.6	53.7	75.7	50.9	69.4	14.3	73.4	81.8
Diene, %	54.4	40.1	32.4	23.9	21.7	30.2	10.0	32.4	16.0	75.5	17.0	8.3
Triene, %	8.1	3.7	1.5	0.8	0.7	1.6	0.0	1.8	0.1	0.0	0.0	0.0
IV[d]	135	115	104	95.3	93.6	102	82.0	104	87.3	142	92.1	84.3
Selectivity,[e] T/D	....	2.0	2.3	2.5	2.6	2.4	....	2.5	1.7	....	....	....
IR[d]												
trans,[f] %	0	5.3	5.8	6.8	7.1	3.4	9.5	6.5	11.0	0	8.9	11.0
Cloud point, C	....	−8	−6	....	−5	−6	0	−5	−2	....	....	....

[a] Abbreviations: SBO, soybean oil; SFO, safflower oil; benzoate, methyl benzoate-$Cr(CO)_3$; benzene, benzene-$Cr(CO)_3$; cyclo, cyclohexane; T, triene; D, diene.

[b] All runs were made at an initial pressure of 500 psi H_2; runs 1 to 4 were made with a 300 ml autoclave and runs 5 to 10 with a 150 ml autoclave.

[c] Triene determined by alkali conjugation and other fatty acids by GLC and normalized to 100.

[d] Calculated from GLC analyses.

[e] Calculated with digital computer (8) assuming the consecutive reactions: triene → diene → monoene.

[f] As methyl elaidate.

tracted fatty acids (150 C/0.015 mm) resulted in yields of 90–95%. For GLC the distilled acids were methylated in MeOH-BF_3 (8).

Results

Methyl benzoate-$Cr(CO)_3$ and benzene-$Cr(CO)_3$ were used as catalysts in this study because they proved to be the most active among the arene complexes and exhibited optimum thermal stability for the hydrogenation of polyunsaturated fats (4).

Hydrogenation of soybean oil was followed by periodic GLC analyses. Rate curves for a run catalyzed with methyl benzoate-$Cr(CO)_3$ show that the selective formation of monoene corresponds to the disappearance of diene and triene (Fig. 1). Palmitate and stearate remained constant during hydrogenation.

Hydrogenation data obtained with vegetable oils are summarized in Table I. With soybean oil hydrogenated between 145 and 175 C (without solvent), the monoene in the product varied from 42% to 64%, diene from 22% to 40%, and triene from 0.7% to 3.7%. Generally, hydrogenation temperatures exceeding 165 C were necessary to reduce the linolenate level below 2% and the IV to about 100.

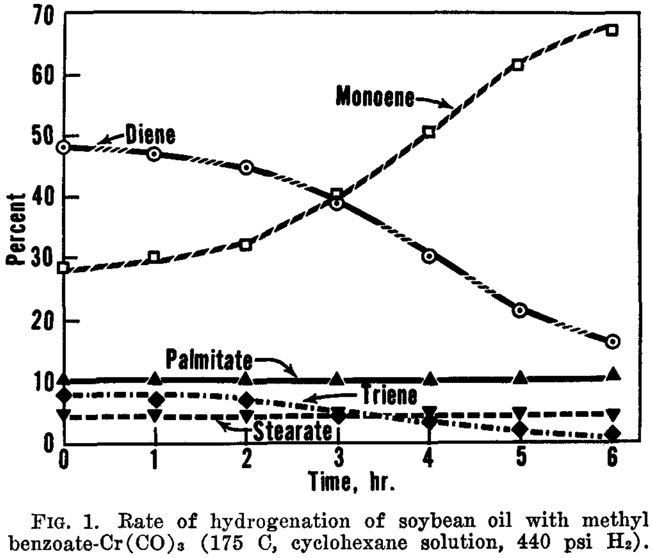

FIG. 1. Rate of hydrogenation of soybean oil with methyl benzoate-$Cr(CO)_3$ (175 C, cyclohexane solution, 440 psi H_2).

In cyclohexane solution more catalyst was apparently needed to obtain the same degree of hydrogenation than when no solvent was used. Methyl benzoate-$Cr(CO)_3$ was a more active hydrogenation catalyst than benzene-$Cr(CO)_3$ (compare runs 5–6 with runs 7–8, Table I). Benzene-$Cr(CO)_3$ was essentially inactive at temperatures below 165 C.

Selectivity values for triene vs. diene hydrogenation varied from 1.7 to 2.6 and seemed to increase with temperature. These values obtained with soybean oils are not so high (3–5) as those with soybean methyl esters (4) and correspond to those generally observed with conventional heterogeneous nickel catalysts (9,10). Although the triene vs. diene selectivity was not unusually high, the diene vs. monoene selectivity was infinitely high because no significant change occurred in saturates.

With safflower oil the diene level was reduced from 76 to 8–17% and the monoene was correspondingly increased from 14 to 74–82%. No change was observed in palmitate or stearate concentrations. Composition of main constituents in hydrogenated safflower oils approximated that of olive oil [saturates 16%, monoenes 65–85%, diene 4–15% (11)].

The *trans* content of hydrogenated oils varied from 5% to 11%. Generally, it was possible to retain 90% to 95% of the *cis* configuration in the products even at IV drops of 50 to 55 in both soybean and safflower oils. Any other hydrogenation catalysts that we have examined so far have produced much higher *trans* levels at corresponding IV drops. All hydrogenated soybean oils were liquid at room temperature. Cloud points varied from 0 to −8 C.

Cleavage analyses of the monoene fractions from two hydrogenated soybean oils showed that 45% to 55% of the double bond remained in the original C_9 position; the rest was distributed mainly between C_{10} and C_{12} positions (Fig. 2). Hydrogenation of pure methyl linoleate and alkali-conjugated linoleate with methyl benzoate-$Cr(CO)_3$ yielded monoenes with double bonds distributed about equally on C_9, C_{10}, C_{11} and C_{12} (12). Therefore the results in Figure 2 indicate that dienes in soybean oil are conjugated before hydrogenation to monoenes by the $Cr(CO)_3$ catalysts. The products of linolenate hydrogenation were apparently not present in suf-

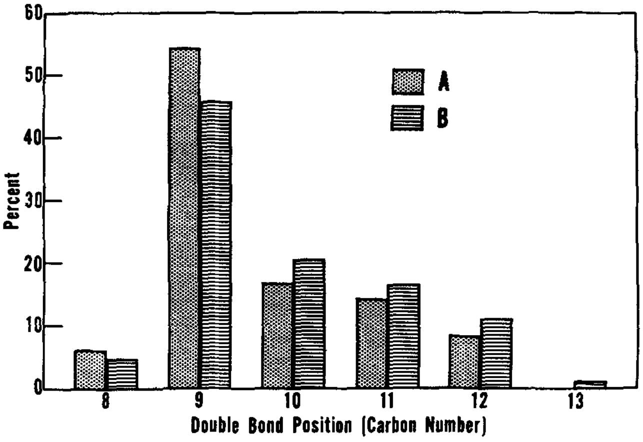

FIG. 2. Double bond distribution in monoene fractions from hydrogenated soybean oils: (A) run 5, Table I; (B) run 6, Table I.

ficiently high concentrations to be detected by the methods of analysis.

Limited studies were made to evaluate the oxidative and flavor stability of soybean oils hydrogenated with methyl benzoate-$Cr(CO)_3$. The hydrogenated and refined oils contained 2–5 ppm chromium (by atomic absorption spectroscopy). AOM stability values and flavor scores of hydrogenated samples were in the same range as those of a commercially hydrogenated-winterized soybean oil which contained antioxidants and methyl silicone (Table II). Added citric acid was apparently sufficient to inactivate any prooxidant effect of residual chromium in the hydrogenated samples. However, a more complete removal of residual chromium would be expected to increase stability and flavor score. These preliminary results indicate that the hydrogenated oils may be suitable as salad oils, however, additional studies are needed to evaluate these oils more completely. More effective means of removing residual chromium in the hydrogenated oils should also be investigated.

Fatty acids were obtained by saponification of hydrogenated soybean and safflower oils. Analyses showed that their composition was about the same as that of commercial oleic acid (Table III). The *trans* content (7–11%) was sufficiently low so that the acids were liquid at room temperature. From their physical characteristics these predominantly *cis* monoene fatty acids appear suitable for industrial uses.

TABLE II

Oxidative and Flavor Evaluations of Soybean Oil Hydrogenated With Methyl Benzoate-$Cr(CO)_3$[a]

Evaluations	SBO + CA[b]	Run 11 + CA[b]	Run 12 + CA[b]	Run 13 + CA[b]	HWSBO[c]
Analyses[d]					
Palmitate, %	10.3	11.9	10.2	11.0	8.4
Stearate, %	4.1	4.7	4.2	4.5	5.3
Monoene, %	23.1	53.7	66.1	68.5	48.4
Diene, %	54.4	27.7	18.2	15.0	35.2
Triene, %	8.1	2.0	1.3	1.0	2.7
IV	135	98.9	91.4	87.1	109
trans, %	0	6.2	8.6	10.9	12.7
Chromium, ppm	0	2.6	1.7	5.4	....
AOM					
PV at 8 hr	3.3	3.7	2.4	2.0	2.3
Flavor score[e]					
Initial	8.1	8.9	7.8	8.3	7.1
4 days, 60 C	6.6	6.4	7.2	6.8	6.5
8 days, 60 C	5.4	5.6	....	....	6.3
Heat test, 200 C[f]	2.5	4.2	....	....	3.9

[a] Conditions: 1.1% catalyst, 175 C, 500 psi H_2; run 11: 900 g oil, 2 liter autoclave, 2 hr; run 12: 600 g oil, 1 liter autoclave, 4 hr; run 13: 900 g oil, 2 liter autoclave, 6 hr.

[b] Plus 0.01% citric acid.

[c] Commercially hydrogenated-winterized soybean oil containing BHA, BHT and methyl silicone (according to label).

[d] See footnote c, Table I.

[e] By the procedure of Moser et al. (13).

[f] Oil was heated to 200 C shortly before panel evaluation.

TABLE III

Fatty Acids From Vegetable Oils Hydrogenated With Methyl Benzoate-$Cr(CO)_3$

Analyses[a]	Soybean oil		Safflower oil		Commercial oleic acid[b]
	A	B	A	B	
Acid value	201	200	198	199	189–204.
Free fatty acids (% oleic)	102	101	100	100	95–103
Saponification value	190	192	196	196	193–206
Saturates, %	16.3[c]	16.3[c]	9.7[c]	10.8[c]	8– 12[d]
Monoene, %	75.5	66.7	72.6	83.1	79– 88[e]
Diene, %	8.2	17.0	17.7	6.1	4– 8
Triene, %	0	0	0	0	0– 1
IV	78.7	86.4	92.6	81.6	83– 95
trans, %	7.0	7.9	8.9	11.0	5– 6[f]

[a] After vacuum distillation of acids.

[b] Emersol (15).

[c] Palmitic and stearic acids.

[d] Myristic, palmitic, margaric and stearic acids.

[e] Myristoleic, palmitoleic and oleic acids.

[f] Typical values reported by private communication (Gerhardt, E. N., Emery Industries, Inc., Cincinnati, Ohio).

Discussion

The $Cr(CO)_3$ complexes form a new class of selective homogeneous catalysts, which are unique in their ability to reduce polyunsaturates to *cis*-monounsaturates predominantly without formation of saturates. Although these catalysts are not so selective as copper for linolenate hydrogenation (15), they do produce much less *trans* unsaturation. High-monoene oils obtained by copper hydrogenation contained 17% to 32% *trans* unsaturation (16), whereas the corresponding product prepared by chromium carbonyl hydrogenation had less than 10% *trans*.

The question arises: Why do the $Cr(CO)_3$ complex catalysts produce mainly *cis* unsaturated products? An attempt to answer this question was made by studying the hydrogenation of model diene compounds. Hydrogenation of methyl *trans,trans*-9,11-octadecadienoate yielded 92% *cis*-10-octadecenoate (12) which is the 1,4-addition product. Deuteration studies also provided direct evidence that 1,4-addition is the dominant path of reduction catalyzed by $Cr(CO)_3$ complexes (17). A cisoid diene-chromium dihydride carbonyl complex was postulated as an intermediate in the hydrogenation. With this intermediate the 1,4-addition monoene product would be expected to assume the *cis* configuration.

We have used these $Cr(CO)_3$ catalysts to hydrogenate soybean and safflower oils and have obtained high *cis* oils. Our preliminary flavor and oxidative stability evaluations indicate that the hydrogenated oils (IV 90–100) may be suitable as salad oils. However, for food uses further studies are needed to evaluate edibility and flavor stability of these hydrogenated oils. Oleic acid concentrates were also prepared by saponification of hydrogenated oils (IV 80–90). These acids are liquid and do not require further fractionation as is done with fatty acids derived from animal fat sources. They would be suitable for industrial uses.

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