Stereoselective Hydrogenation of Model Compounds and Preparation of Tailor-Made Glycerides With Chromium Tricarbonyl Complexes[1]

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Abstract

Studies on the mechanism of stereoselectivity of chromium tricarbonyl catalysts with model compounds provided the basis for the preparation of simulated fats. These synthetic fats were prepared by taking advantage of the unique property of chromium carbonyl complexes to catalyze hydrogenation of polyunsaturates to cis-monounsaturates. Oils simulating the composition of peanut oil were produced by hydrogenating soybean oil stereoselectively to an IV of 94. Simulated olive oil was made the same way from either soybean or safflower oil hydrogenated to an IV of 82–84. Stereoselective 1,4-reduction of eleostearate in tung oil produced oils that had a high proportion of linoleate and that simulated safflower oil. The oleo-disaturated glyceride structure of cocoa butter was also simulated by selectively hydrogenating linoleate in cottonseed oil stearines and in fractionated high-palmitate stearines. Dilatometric and chromatographic studies showed that the cis-monoene-disaturated glyceride is the major component (60–70%) in the synthetic cocoa butter.

Introduction

The preparation of synthetic fats simulating the fatty acid composition of natural, edible fats and oils has been a long sought objective in fat chemistry. Readily available vegetable oils may be utilized to advantage by converting them into tailor-made glycerides that may be in greater demand or more desirable economically or nutritionally than the original fats.

Methods to synthesize certain glyceride structures (1–3) are not only difficult and elaborate but often impractical to carry out on a reasonably large scale. A more practical approach is the selective hydrogenation of polyunsaturated fatty acid components in vegetable oils to prepare glyceride mixtures simulating the composition of other less readily available fats. For this purpose, hydrogenation catalysts should promote no rearrangement of fatty acids within the glyceride structure, and a minimum of isomerization of double bonds. Generally, no acyl migration of fatty acids occurs during hydrogenation with conventional heterogeneous catalysts (4). However, catalytic hydrogenation is always accompanied by geometric and positional isomerization of double bonds and usually by formation of saturated products (5). The degree of double bond isomerization is accentuated when hydrogenation is carried out under so-called selective conditions (6).

A new approach to selective hydrogenation has been the use of soluble organometallic compounds as catalysts. A large number of fat-soluble organometallic complexes have been discovered which are selective for the hydrogenation of polyunsaturates without formation of saturates (7). These catalysts also promote the formation of geometric and positional isomers in the hydrogenated products. We discovered that arene-chromium carbonyl complexes are not only selective in hydrogenating conjugated diene and triene fatty esters (8) but also highly stereoselective in catalyzing hydrogenation of polyunsaturates to cis-monounsaturates as main products (9,10).

We have prepared several simulated fats by taking advantage of the unique stereoselectivity of chromium carbonyl complexes. This paper reviews our studies on stereoselective hydrogenation catalyzed by chromium carbonyls as applied to the preparation of various synthetic fats. Oils simulating the composition of vegetable oils were prepared from other fats: olive oil from either soybean or safflower oils; peanut oil from soybean oil; and safflower oil from tung oil. A cocoa-butterlike product was prepared from cottonseed oil stearines. More detailed accounts have been or will be published separately (10; Frankel et al., unpublished). But first, basic studies with model substrates will provide a background for the practical preparation of simulated fats.
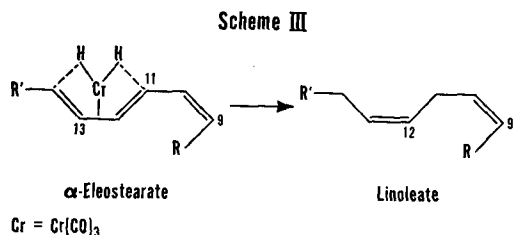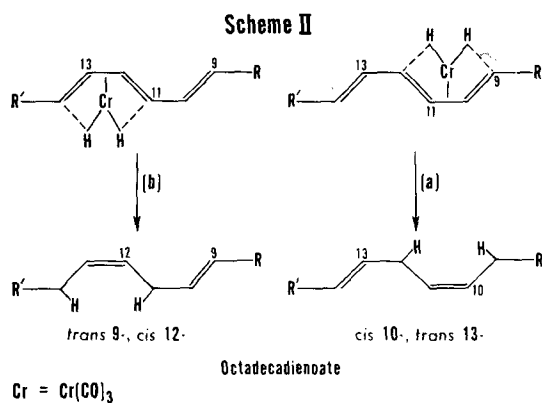
Hydrogenation of Model Compounds

The hydrogenation of model diene compounds was studied to determine why $Cr(CO)_3$ complex catalysts produce mainly cis unsaturated products. Methyl sorbate (methyl 2,4-hexadienoate) is a convenient substrate because its hydrogenation products can be readily determined by gas liquid chromatography (GLC) (11). Methyl 3-hexenoate is the major hydrogenation product obtained in yields of 90% to 99% (8). We have shown by deuterium tracer studies that the reduction of methyl sorbate catalyzed by methyl benzoate-$Cr(CO)_3$ proceeds by 1,4 addition of hydrogen (12). The product obtained with deuterium was identified as methyl 2,5-dideuterio-cis-3-hexenoate (II). A cisoid diene-$d_2Cr(CO)_3$ complex (I) was postulated as intermediate in the reduction (Scheme I).

Scheme I
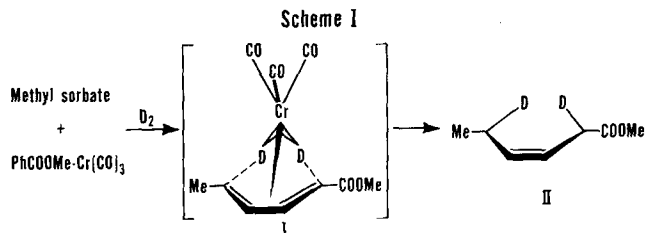
Arene-$Cr(CO)_3$ complexes are highly selective for the hydrogenation of conjugated dienes and trienes (8). In dehydrated methyl ricinoleate the conjugated dienes fatty esters were completely reduced to monoenes, but the nonconjugated dienes were unaffected. Competitive hydrogenation studies showed

Scheme II

trans 9-, cis 12-   cis 10-, trans 13-

Octadecadienoate

Cr = Cr(CO)₃

Scheme III

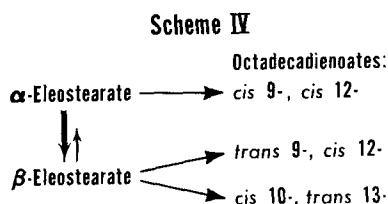α-Eleostearate   Linoleate

Cr = Cr(CO)₃

that in an equal mixture alkali-conjugated methyl linoleate (mainly 9,11- and 10,12-dienes) reduced 22 times faster than methyl linoleate (13). The arene-Cr(CO)₃ catalysts were also highly stereoselective for trans,trans-9,11-dienes (relative rates: cis,cis 1.0; cis,trans 8.0; and trans,trans 25).

The stereoselectivity of these catalysts was further demonstrated by the finding that methyl trans-9,trans-11-octadecadienoate yields essentially only the 1,4 addition-product Δ¹⁰ monoene; whereas the corresponding cis,trans-diene gives a mixture mainly of Δ⁹ and Δ¹⁰ monoenes (Fig. 1). The cisoid diene-H₂Cr(CO)₃ complex (see I, Scheme I) postulated as intermediate in the hydrogenation accounts for the cis configuration of the 1,4 addition monoene products.

Hydrogenation of methyl β-eleostearate with various Cr(CO)₃ complexes yields mainly a mixture of (cis, trans/trans,cis-) 9,12- and 10,13-octadecadienoates (8; Frankel, unpublished). This result indicates that reduction occurs by 1,4 addition of hydrogen at C-9 and C-12 (path a, Scheme II), and at C-11 and C-14 (path b) of β-eleostearate.

The stereoselective 1,4 reduction of the trans,trans-11,13-diene component of methyl α-eleostearate (at C-11 and C-14) would be expected to give methyl linoleate as the only product (Scheme III). However, the products actually obtained with Cr(CO)₃ complex catalysts were a mixture of (cis,trans/trans,cis-) 9,12- and 10,13-octadecadienoates and cis,cis-9,12-octadecadienoate (Frankel, unpublished). Therefore some stereoselectivity was lost by the apparent conversion of α- to β-eleostearate during catalytic hydrogenation by Cr(CO)₃ complexes. The overall reaction sequence, which accounts for the products, may be written as shown in Scheme IV.

Scheme IV

Octadecadienoates:

α-Eleostearate ⟶ cis 9-, cis 12-

β-Eleostearate ⟶ trans 9-, cis 12-
β-Eleostearate ⟶ cis 10-, trans 13-

Hydrogenation of methyl linolenate with methyl benzoate-Cr(CO)₃ yields dienes in which the double
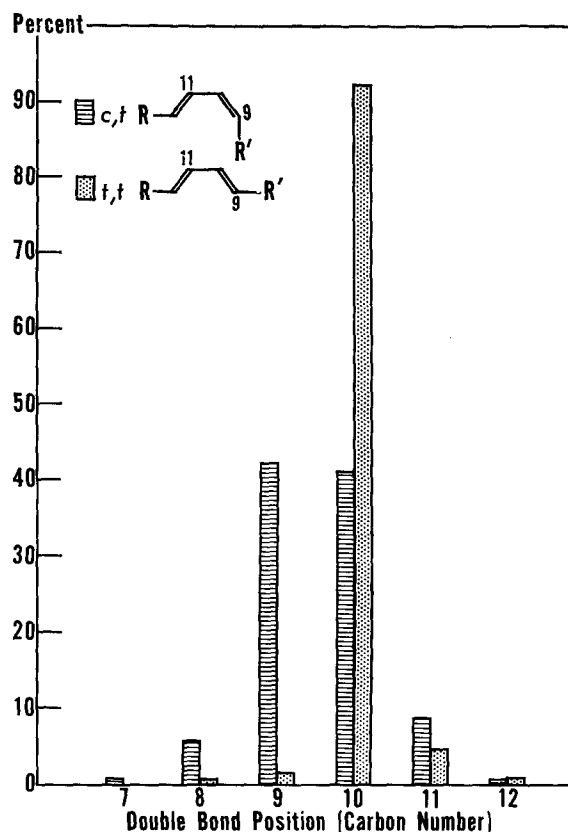

FIG. 1. Double bond distribution in monoenes from methyl cis,trans- and trans,trans-9,11-octadecadienoates hydrogenated with benzene-Cr(CO)₃ (13).

bonds are separated by several methylene groups (Frankel, unpublished). These dienes are only 2% to 25% conjugatable with alkali compared to 90% to 100% with those dienes obtained from hydrogenated eleostearate. The monoene products from linolenate consist of a mixture of cis and trans isomers with double bonds scattered between C-8 and C-15. Competitive hydrogenation studies showed that in an equal mixture methyl β-eleostearate is reduced about 10 times faster than methyl linolenate.

Stereoselective Hydrogenation

Soybean and Safflower Oils

The Cr(CO)₃ complexes of methyl benzoate and benzene were used to hydrogenate soybean and safflower oils to make high-cis oils (10). Oils simulating the composition of peanut oil were prepared by hydrogenating soybean oil stereoselectively to an IV of 95 (Table I). The composition of olive oil was simulated in the products obtained from soybean oil and from safflower oil hydrogenated to an IV of 82 to 84. The trans content (7–11%) was sufficiently

TABLE I

Simulated Peanut and Olive Oils From Soybean and Safflower Oils Hydrogenated With Methyl Benzoate-Cr(CO)₃[a]

Analyses, %	Hydrogenated soybean oils[a]		Hydrogenated safflower oil[a]	Peanut oil[b]	Olive oil[b]
	A	B			
IV	95.3	82.0	84.3	84–100	77 –94
Palmitate	10.3	10.2	7.0	6– 9	7 –16
Stearate	4.3	4.1	2.9	3– 6	1 – 3
Other saturates	0.0	0.0	0.0	1– 4	0.1– 2
Monoene	60.7	75.7	81.8	53– 73	65 –85
Diene	23.9	10.0	8.3	13– 27	4 –15
Triene	0.8	0.0	0.0	....	....
Trans	6.8	9.5	11.0	....	....

[a] Hydrogenations and analyses described previously (10).
[b] From Swern (14).

TABLE II

Simulated Safflower Oils From Tung Oil Hydrogenated With Cr(CO)₃ Complexes

Analyses,[a] %	Hydrogenated tung oils			Safflower oil[e]
	A[b]	B[c]	C[d]	
IV	154.5	147.8	150.2	140–150
Palmitate	1.8	3.2	3.6	3– 6
Stearate	2.3	2.8	2.6	1– 4
Monoene	12.2	15.1	13.1	13– 21
Cis,cis-diene	63.8	56.0	56.9	73– 79
Cis,trans-diene	19.4	21.1	22.1	....
Conjugated diene	0.5	1.8	1.7	....

[a] GLC and IR (10). Diene is all methylene-interrupted as shown by alkali conjugation; cis,trans-diene determined by IR as cis-9,trans 12-octadecadienoate; cis,cis-diene = total diene (GLC)-cis,trans-diene (IR). AgNO₃-TLC showed the absence of trans,trans-diene.
[b] Ethyl benzene-Cr(CO)₃, 175 C, 700 psi H₂, cyclohexane 5 hr.
[c] Methyl benzoate-Cr(CO)₃, 160 C, 440 psi H₂, n-hexane 1 hr.
[d] Cycloheptatriene-Cr(CO)₃, 125 C, 200 psi H₂, n-hexane 4 hr.
[e] From Swern (15).

TABLE III

Simulated Cocoa Butters From Cottonseed Oil Stearines Hydrogenated With Methyl Benzoate-Cr(CO)₃

Analyses,[a] %	Hydrogenated[b]				Cocoa butter[c]
	Nonfractionated stearines		Fractionated stearines		
	A	B	A	B	
IV	44.6	48.5	38.0	37.8	36.7
Palmitate	49.0	47.3	58.0	58.9	24.4
Stearate	2.2	2.2	1.0	1.3	35.4
Monoene	45.5	44.4	37.6	35.5	38.1
Diene	3.3	6.1	3.4	4.3	2.1
Trans	4.8	2.2	7.2	2.5	......
Melting range,[d] C	20–35	25–35	30–40	25–40	25–35
Maximum thermal expansion,[d] ml/5 C/100 g (temp. C)	1.7(30)	2.5(31)	5.1(35)	4.2(35)	6.3(33)

[a] GLC and IR (10), dilatometry (18).
[b] Methyl benzoate-Cr(CO)₃, 175 C, 500 psi H₂, no solvent.
[c] Swern (16).
[d] From differential dilatometric curves (18).

low so that the hydrogenated products were liquid at room temperature. Oxidative and flavor stability as well as cloud points of these hydrogenated oils indicated that they would be suitable for salad use (10).

Tung Oil

The conversion of eleostearate into a mixture of methylene-interrupted dienes (8; Frankel et al., unpublished) suggested that stereoselective hydrogenation of tung oil would provide a means of preparing an oil simulating the composition of safflower oil. The hydrogenation of α-eleostearin in tung oil with Cr(CO)₃ complexes was more stereoselective than that of the corresponding methyl ester. Products contained 77% to 83% methylene-interrupted diene (Table II). The ratio of cis,cis- to cis,trans-diene varied from 2.6 to 3.3. With methyl α-eleostearate this ratio varied from 0.4 to 0.5. Therefore, the tendency of α-eleostearin to isomerize to β- is apparently less in tung oil than in the methyl ester. The high selectivity of the catalysts for eleostearate permits the reduction of triene to diene with only a small conversion further

to monoene. The products which best simulated the composition of safflower oil were obtained when hydrogenation was judiciously stopped so that eleostearate was completely reduced and methylene-interrupted dienes reached a maximum value (Fig. 2). If the hydrogenation is continued beyond this point, then the diene is further reduced to monoenes. The catalytic activity of cycloheptatriene-Cr(CO)₃ at lower temperatures (120–130 C) than methyl benzoate-Cr(CO)₃ (160–170 C) permitted a greater accumulation of dienes in tung oil (Fig. 2).

Cottonseed Oil Stearines

Many attempts have been made previously to simulate the structure of cocoa butter, which contains approximately 80% oleo-disaturated glycerides (16). This unique structure results in a sharp melting range and imparts a characteristic brittleness. A 1969 patent describes the preparation of synthetic confectionary fats by selective hydrogenation of cottonseed oil stearines followed by fractional crystallization
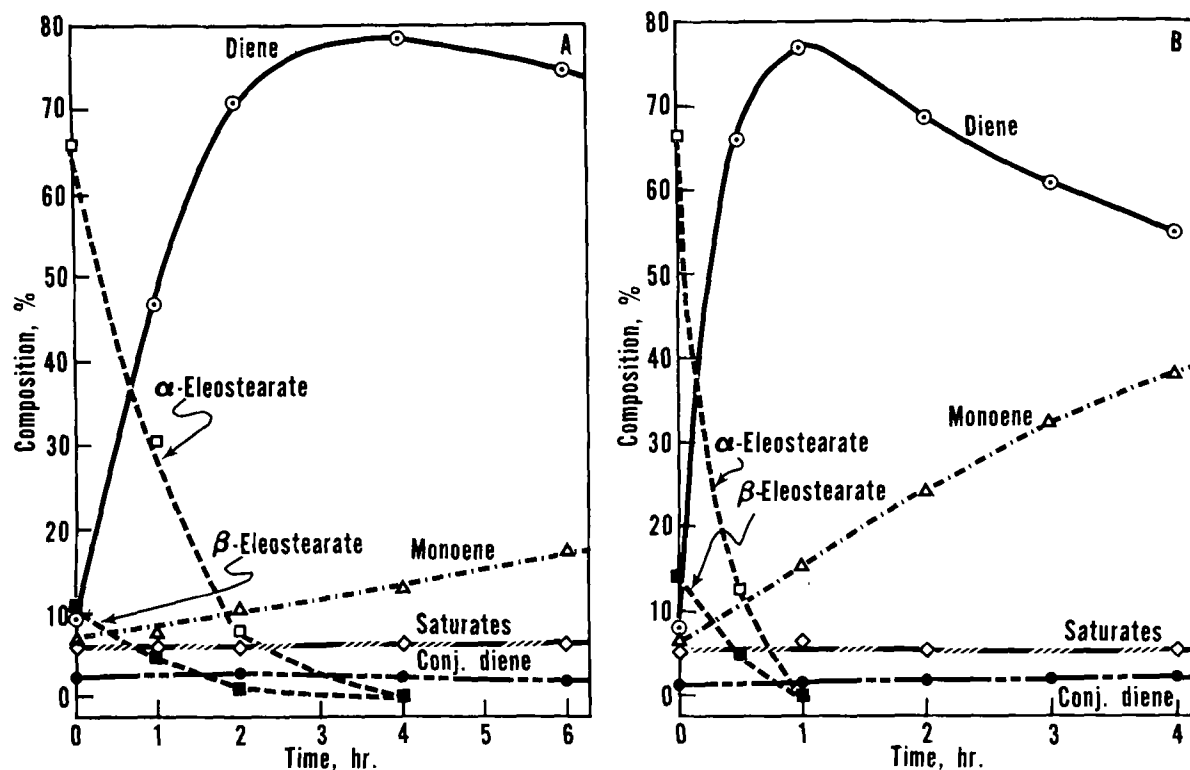

FIG. 2. Rate of hydrogenation of tung oil with: (A) cycloheptatriene-Cr(CO)₃ (125 C, 220 psi H₂) and (B) methyl benzoate-Cr(CO)₃ (160 C, 440 psi H₂) (Frankel et al., unpublished work).

(17). The stearines were hydrogenated with a zirconium-promoted nickel catalyst at 84 C. Although *trans* content of the products reportedly ranged from 10.2% to 10.7%, the stearate increased significantly (6–12%). Fractionation by crystallizing and solvent leaching was necessary to remove trisaturated glycerides from the hydrogenated stearines.

We prepared synthetic cocoa butter by stereoselective hydrogenation of stearines from winterized cottonseed oil. The use of chromium carbonyl catalysts caused a minimum of *trans* isomerization and no formation of saturates. To prepare products simulating the fatty acid composition of natural cocoa butter, it was necessary to fractionate the cottonseed oil stearines before hydrogenation to increase the level of palmitate. Repeated crystallization of petroleum ether solutions of stearines at 0 F yielded fractions (about 30%) containing 56% to 60% palmitate. These fractions were then hydrogenated stereoselectively with methyl benzoate-Cr(CO)₃. Analyses in Table III show that fractionated cottonseed oil stearines gave hydrogenated products in which the palmitate and monoene content corresponded to the saturate and oleate in cocoa butter; *trans* values ranged from 2% to 7%. The hydrogenated stearines melted in the same range as cocoa butter, whereas the fractionated hydrogenated stearines melted about 5 C higher. However, dilatometric curves showed that the fractionated hydrogenated stearines have a narrow and more pronounced temperature range maximum than the nonfractionated samples. The sharpness of the dilatometric curve of these samples compares favorably with that of cocoa butter. These results suggest that the disaturated glycerides of the hydrogenated fats are similar in melting characteristics to those of cocoa butter. Tri-glyceride analyses by AgNO₃-TLC (Frankel et al., unpublished) showed that the *cis*-monoene-disaturated glyceride component ranges from 60% to 70% in the synthetic cocoa butter. Therefore, a satisfactory confectionary fat may be prepared by stereoselective hydrogenation of fats containing a sufficient amount of saturates so that the monoene-disaturated glycerides become the main constituent.

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