Technical

Catalytic Hydrogenation of Vegetable Oils: II. The Activity of the Prereduced Copper Chromite Catalyst[1]

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ABSTRACT

The prereduction of copper chromite with hydrogen produces a strong deactivation of catalyst in *soybean oil* hydrogenation at 200 C and 6 atm. ESCA studies and kinetic data show that the decrement of the activity is correlated to the disappearance of Cu'' and Cu' species and to the decrement of Cu/Cr ratio on the catalyst surface. The comparison of activity between original and prereduced catalysts allows a better elucidation of the role of Cu' in promoting the double bond conjugation and of Cu^0 in catalyzing the conjugated double bond hydrogenation.

INTRODUCTION

The copper oxide-chromium oxide system (1) has been extensively studied in the past due to the high selectivity shown by this catalyst in the partial hydrogenation of vegetable oils (2-4). In particular, many experiments have been done to correlate catalytic properties with operational parameters such as temperature (5), hydrogen pressure (5-9), hydrogen flow (10), catalyst concentration (7,9), substrate composition (8,11) and activation procedures (12,13).

At the same time, much attention has been devoted to the characterization of the active centers present in the catalyst: different techniques, such as X-ray diffraction analysis (14-16), electron spectroscopy for chemical analysis (ESCA) measurements (14,17,18) and differential thermal analysis (DTA) determinations (19) have been used along with chemical analysis for studies of the bulk and surface properties. According to recent work, Cu^0, in intimate contact with $Cu_2Cr_2O_4$, seems to be the active species for the linolenate and linoleate hydrogenation (8,14) which proceeds via double bond isomerization (5,20,21).

One point subject to much speculation is the observation that the catalyst activity decreases with time (14). This behavior has been attributed to the variation of the relative concentrations of Cu^0 and Cu' species formed during catalyst reduction (8,14).

However, much less attention has been given to the catalyst activity toward conjugated polyenes. In fact, limited kinetic data given in the paper of Koritala and Selke, who observed deuterium-hydrogen exchange and double bond isomerization during the deuteration of conjugated dienes (11), do not allow any comparison between these substrates and the nonconjugated analogs.

Also little studied were the activity and the selectivity of prereduced copper chromite catalysts which show a higher content of Cu^0 on the surface than those obtained by reduction in the presence of the substrate.

These observations prompted us to extend our previous studies on the selective hydrogenation of polyenes (22,23) to the copper oxide-chromium oxide system to elucidate the role of copper, in different oxidation states, as catalyst for the hydrogenation of nonconjugated and conjugated isomers of fatty acid molecules.

EXPERIMENTAL PROCEDURES

The catalyst normally used was a modified commercial copper chromite (GIRDLER G-89) supplied by Sud-Chemie A.G., with the following composition: 37.1% Cu, 27.4% Cr and 0.78% Mn. ESCA measurements also were carried out on an Mn-free copper chromite containing only the phases CuO and $CuCr_2O_4$ (GIRDLER G-13). The catalysts were heated at 350 C in air for 6 hr before use.

Soybean oil was a refined and bleached commercial product, with the following gas liquid chromatographic (GLC) composition: C16:0=11.5%; C18:0=3.5%; C18:1=23.2%; C18:2=54.7%; C18:3=7.1%.

Soybean oil methyl esters were prepared by transesterification with methanol catalyzed by sodium methoxide, and purified by distillation under reduced pressure.

Soybean oil conjugated methyl esters were prepared by a slightly modified analytical method (24): in a stainless steel autoclave (150-mL) 10 g soybean oil, 6 g NaOH and 100 mL CH_3OH were heated at 190 C for 3 hr under nitrogen atmosphere with magnetic stirring. After cooling, the soapy paste was transferred into a 2L flask and 1 L of H_2O was added. The resultant solution was treated with diluted H_2SO_4 (1:10, v/v) in slight excess. The free fatty acids were extracted with petroleum ether and dried over Na_2SO_4. After solvent evaporation, the methyl esters were obtained by esterification with a BF_3/CH_3OH solution, and purified by distillation under reduced pressure (conjugated dienes = 32.7% by ultraviolet [UV] analysis).

Reduction of Copper Chromite with Hydrogen

A sample (0.1-1 g) of G89 or G13 catalyst was introduced into a glass reactor which had a long, air-cooled neck, and heated for 0.5 hr under vacuum at 270 C in a thermostatic device. Then hydrogen at 0.9-1 atm was carefully introduced.

A fast reduction took place as indicated by the water condensation on the cold arm of the reactor. From time to time, the condensate was purged under vacuum and, finally, hydrogen was replaced with nitrogen after cooling at room temperature. The reduced catalysts (G89R and G13R) appear as black, finely divided powders that are unstable to atmospheric oxygen. They were handled under nitrogen atmosphere (41.4% Cu; 29.5% Cr and 0.85% Mn for G89R).

Recovery of Used Copper Chromite Catalyst

A sample of G89 or G13 (1.5 g) was suspended in 500 mL of soybean oil and introduced into a 1 L stainless steel autoclave. The temperature was raised, under vacuum, to 200 C and hydrogen was introduced at 6 atm. The mixture

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[1] For part I, see ref. 23.

was stirred at 600 rpm for a suitable time (1.5 hr for the catalyst referred to in the text as G89U) at constant hydrogen pressure. The autoclave was then rapidly cooled to 80 C, the slurry transferred under nitrogen atmosphere into a 1.5 L flask and diluted with 500-mL of dried, deaerated petroleum ether. The solid, collected in a paper thimble, was purified in a Sohxlet apparatus by extraction with petroleum ether under nitrogen atmosphere and dried under vacuum.

Hydrogenation Reactions

A mixture of catalyst and deaerated substrate was introduced under vacuum into a preheated, stainless steel autoclave (150 mL) provided with magnetic stirring and a sampling device. Hydrogen was then introduced at suitable pressure and stirring was started. During the reaction, the pressure was kept constant by supplying hydrogen.

Reactions at atmospheric pressure were carried out in an all-glass reactor which was connected, through a water-cooled arm, to a gas burette. Detailed experimental conditions are reported in the tables and figures.

Analytical Methods

The methyl esters from soybean oil were analyzed with a Hewlett Packard 5880A gas chromatographic apparatus using a 6 ft X 1/8 in. stainless steel column packed with 10% EGSSX on 100/120 Chrom P.

C_{18} methyl esters, purchased from C. Erba, were used as standard.

The amount of conjugated polyenes was evaluated by a UV method (24) using a Cary 219 UV spectrophotometer.

The metal content of the bulk of the catalysts was determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer 305 instrument. The samples were dissolved by wet digestion with boiling concentrated perchloric acid.

X-ray photoelectron (XPE) spectra were done using a Vacuum-Generator ESCA 3 spectrometer with Al K source ($h\nu$ = 1486.6 eV). Binding energies were referred to the Au $f_{7/2}$ (b.e. = 84.0 eV) and C 1s (b.e. = 285.0 eV) was used as internal standard for calibration and correction of charging effects (25).

RESULTS AND DISCUSSION

Catalytic systems having different surface amounts of Cu$^{\circ}$ and Cu$'$ can be obtained by sampling the copper chromite catalyst (Girdler–G89 or G13) during the hydrogenation of soybean oil at 200 C and 6 atm of H_2.

ESCA measurements obtained by us (26-28) on such samples are consistent with the data previously reported (14-18).

Thus, a fast reduction of Cu$''$ during the use of G13 and G89 catalysts is shown by the shift of Cu2P binding energies to low values (Table I) and by the gradual disappearance of the satellite structure (Fig. 1). In addition, the presence of separated peaks, ca. 2.3 eV, in Auger LMM (25) spectra of used G13 and G89 indicates the formation of Cu$'$ and Cu$^{\circ}$ species.

In fact, such a separation has been observed in the case of pure samples of Cu metal and Cu_2O (27,28). The Cu$^{\circ}$ species increases during the hydrogenation reaction, as shown by the relative peak intensities (Fig. 2), although a small amount of Cu$'$ is still present even after a long reaction time (120′). This agrees with studies of other authors who have found ca. 5% of Cu$'$ in catalysts used for similar long times (8,14).

In the case of Mn-free catalyst, G13, we also derived information on the surface dispersion of copper. In fact,

Table I

Experimental Binding Energies and CuLMM Auger Kinetic Energies (eV)

Catalyst	Cu $2P_{3/2}$	Cu satellites ΔE	Cu satellites %	CuLMM	Cu/Cr[a]
G13	934.8(3.5)[b]	7.5	45	917.9	1.1
G13U(30)[c]	933.0(2.7)			916.5	0.9
G13U(60)	932.8(2.6)			917.4	0.8
G13U(120)	932.8(2.8)			918.1	0.7
G13R	932.6(2.0)			918.4	0.5
G89	934.7(3.8)	7.7	45	917.6	
G89U(30)	933.0(2.5)			916.7	
G89U(60)	932.9(2.3)			917.2	
G89U(120)	932.8(2.3)			917.7	

[a] Atomic ratio on the surface of the catalyst.
[b] Full width at half maximum of the peak.
[c] Time after which the catalyst has been recovered.

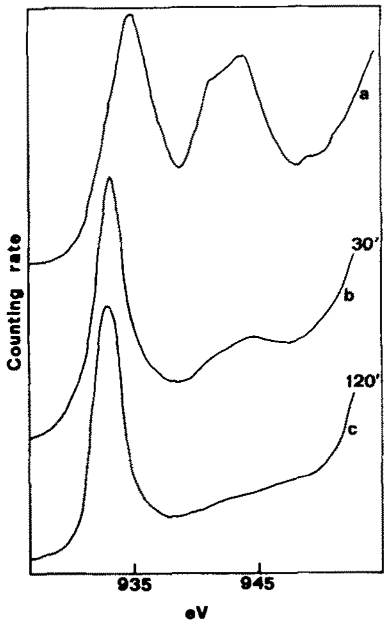

FIG. 1 The Cu2P spectra for fresh G89 (a) and for G89U recovered from soybean oil after 30 min (b) and 120 min (c) of reaction (200 C, 6 atm H_2 and 0.3% catalyst).

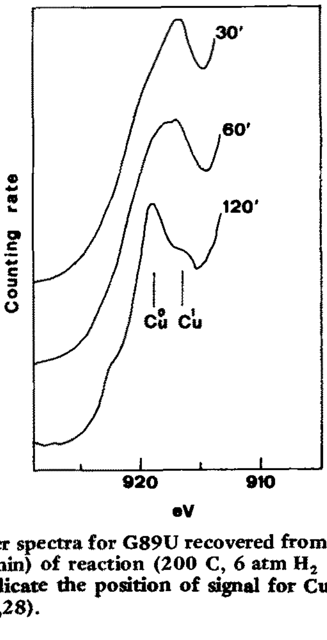

FIG. 2. Cu Auger spectra for G89U recovered from soybean oil after various times (min) of reaction (200 C, 6 atm H_2 and 0.3% of catalyst). Marks indicate the position of signal for Cu metal (Cu$^{\circ}$) and Cu_2O (Cu$'$) (27,28).

the signal intensities in Cr2P and Cu2P XPE spectra show that the molar ratio total Cu/total Cr on the surface decreases with reaction time from 1.1 in the fresh catalyst to 0.7 in the 2-hr used sample (Table I), whereas the analysis on the bulk ensures a constant ratio.

Therefore, the modification of the dispersion degree of copper on the catalyst is shown by ESCA technique as an apparent decrement of total amount of the copper on the surface.

The growth of Cu^{0} crystallites, which become thicker as the reaction time proceeds, can be responsible for the above observations and suggests a new integrative interpretation for the decrement of catalytic activity, which was ascribed by other authors only to the variation of the Cu^{0}/Cu$'$ ratio (14).

A much higher Cu^{0} content on the catalyst surface can be obtained when copper chromite is treated with hydrogen at high temperature in the absence of substrate. In fact the black, air-sensitive samples of G89 and G13 prereduced at 270 C and 1 atm (G89R and G13R) do not show (Fig. 3) any more detectable amount of Cu$'$ on the surface by the Auger LMM technique (27,28). In these prereduced copper chromite catalysts (G89R and G13R), we also observed by XPS technique, a molar Cu/Cr ratio decrement from 1.1 to 0.5, which is greater than that evaluated for the used catalysts (Table I) (28).

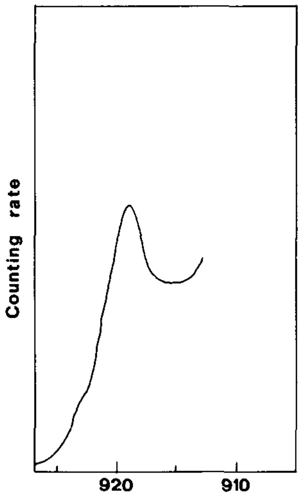

FIG. 3. Cu Auger LMM spectrum for G89R catalyst obtained by treating fresh G89 at 270 C with hydrogen at atmospheric pressure for 30 min.

The strongly exothermic reaction which leads to the reduced catalysts must be accurately controlled to avoid the bulk overheating which induces a subsequent reaction with formation of a gray product that is quite inactive in the polyene hydrogenation. This product shows Cu^{0} and Cr$'''$ on the surface with the lowest observed molar Cu/Cr ratio of ca. 0.4 (the nonuniform composition of the surface of this product does not allow an accurate XPS determination; (C. Furlani et al., private communication).

Black, active catalysts can be obtained by supplying hydrogen slowly and by removing heat with an efficient exchanger.

The catalytic activities of the prereduced (G89R), 1.5-hr used (G89U) and fresh (G89) catalysts have been compared in the dead-end hydrogenation of commercial soybean oil at 6 atm of H_2 and 200 C. Results (Table II) show that the G89R is much less active than G89 and G89U.

To avoid possible specific poisoning effects on reduced catalyst due to secondary components in the oil, we have also used distilled soybean oil methyl esters as substrate. The results for G89R and G89 (Table II) indicate a trend similar to that observed with the oil.

A first point to be outlined in these experiments is the fact that a small amount of Cu$'$ (ca. 5%) besides Cu^{0} (ca. 95%) on the G89U ensures a high catalytic activity compared to that of G89R, for which Cu$'$ is no more detectable. The high catalytic activity of used catalyst has been observed by other authors (14).

A second observation, derived from Figure 4, is that

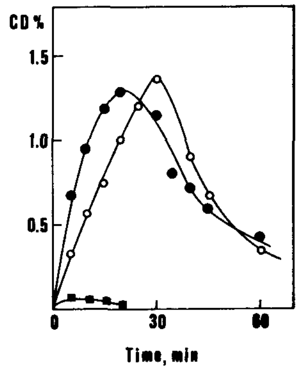

FIG. 4. Amount of conjugated dienes formed during the hydrogenation of soybean oil at 200 C and 6 atm catalyzed by 0.3% w/v of G89 (●), G89U (○) or G89R (■).

TABLE II

Composition of Soybean Oil and Soybean Oil Methyl Esters after Hydrogenation^{a} with Differently Treated Copper Chromite Catalyst

Substrate	Catalyst	Time (hr)	16:0	18:0	18:1	18:2	18:3	IV (GLC)^{b}
Soybean oil	–	–	11.5	3.5	23.2	54.7	7.1	132.5
	G89	1	11.5	3.5	38.4	45.0	1.2	113.6
	G89U	1	11.4	3.6	41.4	42.2	1.7	112.7
	G89R	2	11.5	3.5	24.2	53.8	7.0	131.5
	G89R	10	11.5	3.7	28.7	50.5	5.6	126.1
Soybean oil methyl esters	–	–	11.7	3.5	22.9	54.3	7.6	132.8
	G89	1	11.7	3.5	40.8	42.7	1.2	111.7
	G89R	1	11.7	3.5	23.1	54.2	7.5	132.6
	G89R	10	11.7	3.6	31.1	48.7	4.9	123.3

[a] 0.3% w/v catalyst, 200 C and 6 atm H_2.

[b] IV: iodine value, calculated from GLC data.

the catalysts containing Cu′ species on the surface produce the accumulation of conjugated dienes whereas the catalyst containing only Cu° species does not accumulate these isomers.

A detailed investigation of the UV spectra of reacted and original soybean oil shows further differentiation between the G89R and G89 (Fig. 5). In fact, with G89R, the band at 268 nm due to a small amount of conjugated trienes (29) completely disappears, while the background intensity in the 232 nm region remains substantially unchanged. With G89 catalyst, the band at 268 nm similarly disappears, while a strong band appears at 232 nm, due to conjugated dienes.

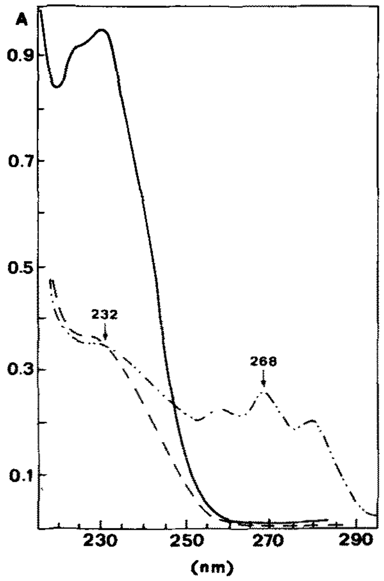

FIG. 5. UV spectra of soybean oil before (—·—) and after hydrogenation (200 C, 6 atm, 0.5 hr) catalyzed by 0.3% w/v of G89 (——) or G89R (– – –).

The above observations suggest that the G89R, although it is almost inactive in the hydrogenation of soybean oil, is active in the hydrogenation of conjugated polyenes.

To confirm this point, we have hydrogenated a solution having a concentration of ca. 3% of conjugated dienes obtained by diluting preconjugated soybean oil methyl esters with Nujol. This solution simulated the concentration of conjugated isomers at the first stage of a reacting soybean oil in the presence of fresh catalyst (Fig. 6).

The G89R and G89 were active even under conditions (140 C, 1 atm H_2) that were milder than those used in the hydrogenation of nonconjugated methyl esters (200 C and 6 atm H_2).

As shown in Figure 6, the reaction takes place without induction time using G89R, whereas with untreated G89, the hydrogenation started only after ca. 2 hr. This induction time is probably due to the formation of the active species Cu′ and Cu°, as in the case of soybean oil (14).

When such mild conditions were used for nonconjugated methyl esters, a much slower hydrogenation rate was observed both with G89R and G89: with a reaction time of ca. 8 hr essentially no reaction took place (drop in IV $< 1\%$).

The experiments just discussed enable us to differentiate more clearly the contribution of Cu′ and Cu° to the overall activity of the copper chromite catalyst in the hydrogenation of vegetable oils. Thus, the strong decrement of activity shown by G89R in soybean oil hydrogenation (Table II) can be ascribed to the low tendency of Cu° to promote the conjugation of two methylene-interrupted double bonds of fatty molecules. Cu°, however, is able to hydrogenate conjugated fatty molecules (Fig. 6) even in absence of Cu′; the Cu′ is essential only in the conjugation step of the hydrogenation reaction (14).

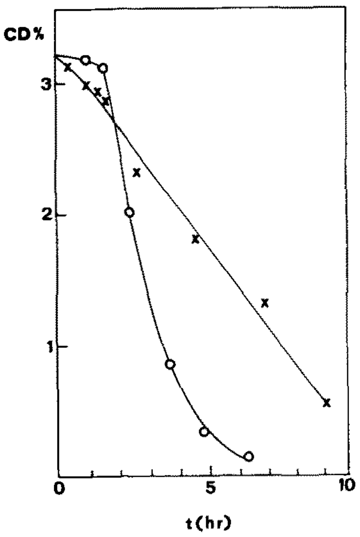

FIG. 6. Amount of conjugated dienes during the hydrogenation of a Nujol solution of soybean oil conjugated methyl esters at 140 C and 1 atm catalyzed by 0.3% w/v of G89 (○) or G89R (x).

The observation that the G89 shows a higher rate (ca. 2 times) that G89R in the hydrogenation of conjugated methyl esters after the induction time (Fig. 6) suggests either a possible assistence of Cu′ species (14) or, more probably, that this effect is due to a higher copper amount on the surface as reflected by molar ratio Cu/Cr by XPS (28) (0.7 for G13U and 0.5 for G13R).

This difference of molar ratio Cu/Cr, however, does not account for the dramatic loss in catalytic activity of G89R in the hydrogenation of soybean oil (and related methyl esters) because a similar drop of activity is not observed with conjugated methyl esters.

The ability of G89 to hydrogenate conjugated trienes of commercial soybean oil, also in the first part of the reaction when conjugated dienes are accumulated (Fig. 5), should be ascribed to a high selectivity toward conjugated trienes along with a low probability of obtaining three conjugated double bond isomerization.

ACKNOWLEDGMENT

This work was supported by Consiglio Nazionale delle Ricerche, Rome (Progetti Finalizzati, Chimica Fine e Secondria). The authors thank C. Furlani, F.M. Capece, V. Di Castro and G. Mattogno for ESCA studies and for the continuous helpful discussion.

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[Received December 3, 1981]

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cis-trans Isomerization of Unsaturated Fatty Acids with *p*-Toluenesulfinic Acid

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ABSTRACT

Elaidination of unsaturated fatty acids using *p*-toluenesulfinic acid yielded 77-80% total *trans* unsaturation in the products. Results from reactions with monoene, diene, and triene isomers indicated that only geometric isomerization takes place. Each double bond isomerized randomly and independently in the polyunsaturated fatty acids. Reactions proceeded quickly, and the method proved convenient and reliable.

INTRODUCTION

Much research has been done to find a convenient method for *cis-trans* isomerization of long-chain fatty acids. Nitrous acid and selenium, although mild reagents, produce byproducts difficult to remove; side reactions and impurities occur more readily with polyunsaturates than with monounsaturates during isomerization (1). Recently, Gibson and Strassburger reported *p*-toleuensulfinic acid as a good reagent to accomplish the geometric isomerization of methyl oleate (2). We have extended the study to include polyunsaturated methyl esters.

EXPERIMENTAL

Pure methyl esters were prepared using counter double current distribution (3). Methyl *cis*-9,*cis*-15 octadecadienoate was prepared by argentation countercurrent distribution of hydrazine-reduced linolenic acid (4). *p*-Toluenesulfinic acid was prepared by acidification of the sodium salts (5).

In the elaidination experiments, which were carried out in a manner similar to those of Gibson and Strassburger (2), 250-mg methyl ester in 10-ml dioxane was added to 20-mg *p*-toluenesulfinic acid and refluxed 15 min. The cooled mixture was diluted with 25-ml 1N NaOH solution, extracted with petroleum ether, and washed twice with saturated NaCl solution, dried, and evaporated. The overall recovery of methyl ester was 88-93%.

Analyses of the elaidinized mixtures were performed on a Perkin Elmer 3920 Gas Chromatograph using a 50 m × 0.25 mm id Silar 10-C glass capillary column. Column temperature was 170 C; the flow rate was 1.06 mL/min through the column and 175 mL/min through the splitter for a split ratio of 165. The amount of *trans* bonds in the isomerized samples was calculated from the capillary gas chromatograph (GC) data and also was determined by AOCS infrared (IR) spectrometric methods (6). Double bond distribution was determined from the sodium borohydride reduced ozonides (7).

RESULTS AND DISCUSSION

Litchfield et al. indicated an equilibrium mixture containing about 75% *trans* isomer was attained with oleic, linoleic, and linolenic acids were elaidinized with nitrous acid or selenium (1). Results in Table I show that *p*-toluenesulfinic acid-catalyzed isomerizations of these fatty acid methyl esters gave approximately the same 75-25 equilibrium mixture.

In agreement with Gibson and Strassburger (2), isomerization of *cis*-9-octadecenoate yielded 79% *trans*. Analysis of both the *trans* and *cis* monoene fractions for positional isomerization showed 100% of the double bond is located at the $\Delta 9$ position.

Two different diene isomers were evaluated, *cis*-9,*cis*-12-octadecadienoate with one methylene group between the double bonds and *cis*-9,*cis*-15-octadecadienoate with 4 methylene groups between the double bonds. Geometric isomers formed during each reaction were identified by comparing equivalent chain length data to values published by Scholfield (8). Total *trans* calculated from GC data is 78% for the 9,12 diene mixture and 79% for the 9,15 diene mixture (Table I). From IR data, the value for the 9,12 diene isomerized mixture was 132% compared to methyl elaidate. A pure sample of methyl *trans*-9,*trans*-12-octa-