TABLE I
GCMS Analysis of C_{11}–C_{14} Chevron Alpha Olefins

Compound	Per cent	Compound	Per cent
1-Hexene	Trace	n-Dodecene (internal)	0.3
		n-Dodecadiene (internal)	0.1
1-Heptene	Trace	C_{12} Cyclopentadiene / C_{12} Cyclic olefin	0.2
1-Octene	Trace	C_{13} Branched olefin	0.3
		C_{12} Cyclic olefin	0.1
1-Nonene	Trace	C_{12} Cyclic olefin	0.2
		C_{12} Cyclic olefin	0.2
n-Decane	Trace		
1-Decene	1.6	n-Tridecane	0.1
C_{10} Cyclic olefin	Trace	1-Tridecene	22.4
C_{10} Cyclic olefin	Trace	1,12-Tridecadiene / C_{13}-Cyclic olefin	0.8
C_{10} Cyclic olefin / C_{11} Branched olefin	0.2	n-Tridecene (internal)	0.2
C_{10} Cyclic olefin / C_{11} Branched olefin	0.3	C_{13}-Cyclic olefin / C_{13}-Cyclic Paraffin	0.1
		C_{13} Cyclic olefin	0.1
n-Undecane	0.1	C_{13} Cyclic olefin	0.5
1-Undecene	19.7	C_{14} Branched olefin	0.1
1,10-Undecadiene / C_{11}-Cyclic olefin	0.8	C_{13} Cyclic olefin	0.1
		C_{13} Cyclic olefin	0.1
n-Undecene (internal)	0.2		
n-Undecadiene (internal)	0.1	n-Tetradecane	0.1
C_{11} Cyclopentadiene / C_{11} Cyclic olefin	0.2	1-Tetradecene	22.4
C_{11} Cyclic olefin	0.2	1,13-Tetradecadiene / C_{14} Cyclic olefin	0.8
C_{11} Cyclic olefin / C_{12} Branched olefin	0.4	n-Tetradecene (internal)	0.2
		C_{14} Cyclic olefin	0.1
C_{11} Cyclic olefin / C_{12} Branched olefin	0.4	C_{14} Cyclic olefin	0.1
		C_{14} Cyclic paraffin	0.2
C_{11} Cyclic olefin	0.2	C_{14} Cyclic olefin	Trace
		C_{14} Cyclic olefin	Trace
n-Dodecane	0.1	C_{14} Cyclic olefin	Trace
1-Dodecene	23.1	n-Pentadecane	Trace
1,11-Dodecadiene / C_{12} Cyclic olefin	0.9	1-Pentadecene	1.5
		n-Pentadecene	0.2

tained by spiking the lower molecular weight fractions with pure α,ω-diolefins.

Table I presents the results of the GCMS analysis of C_{11}–C_{14} Chevron Alpha Olefins. Table II shows the carbon number and group-type breakdown of these GCMS data. This is a complete analysis of the C_{11}–C_{14} Chevron Alpha Olefins utilizing the identifying powers of the mass spectrometer.

TABLE II
Carbon Number Breakdown of GCMS Data from the Analysis of C_{11}–C_{14} Chevron Alpha Olefin

	C_{11}	C_{10}	C_{12}	C_{13}	C_{14}	C_{15}	Totals
1-Olefins							
Straight	1.6	19.7	23.1	22.4	22.4	1.5	90.8[a]
Branched		0.3	0.4	0.3	0.1		1.1
Internal monoolefins							
Straight		0.2	0.3	0.2	0.2	0.1	1.0
Naphthenic	0.3	1.2	0.9	1.2	0.6		4.2
Diolefins							
Alpha, Omega		0.4	0.5	0.5	0.5		1.9
Others		0.2	0.2				0.4
Saturates							
Paraffins	Trace	0.1	0.1	0.1	0.1	Trace	0.4
Cycloparaffins				Trace	0.2		0.2
Totals	1.9	22.1	25.5	24.7	24.1	1.6	

[a] C_9–C_9 1-olefins amounted to about 0.1% in this sample and are included in this total but not in the body of the table.

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Selective Hydrogenation of Soybean Oil with Sodium Borohydride-Reduced Catalysts[1]

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Abstract

The reaction of metallic salts in aqueous solution with sodium borohydride produces finely divided metals that are catalytically active for hydrogenation. Salts of nickel, cobalt, palladium and platinum give active catalysts for the selective hydrogenation of soybean oil. Iron and silver salts, when reduced with sodium borohydride, show no activity at 200C and atmospheric hydrogen pressure. The cobalt catalyst produces the least amount of stearate. Incorporation of palladium, platinum, copper or chromium up to 2% enhance the activity of the nickel catalyst. Copper and chromium salts, when reduced together, form catalysts that hydrogenate linolenyl groups in soybean oil seven times more rapidly than linoleyl groups. No stearate formation is observed with these binary catalysts.

[1] Presented at the AOCS Meeting, Houston, April 1965.
[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

Introduction

THE REDUCTION OF NICKEL salts from aqueous or alcoholic solutions with alkali metal borohydrides produces finely divided metal that possesses catalytic activity for hydrogenation reactions (2,15,16). A sodium borohydride-reduced nickel had excellent "reuse properties" for the hydrogenation of safrole (16). This catalyst contained boron in addition to nickel (15,16). It was suggested that the catalyst corresponds to Ni_2B; later studies indicated the presence of Ni_3B (10). Other catalysts prepared with sodium borohydride included cobalt, copper, platinum, palladium, rhodium, ruthenium, osmium and irridium (3,15). The first 5 of these catalysts also contained varying amounts of boron (15–17).

The simplicity and rapidity with which catalysts can be produced with borohydride have encouraged us to prepare several catalysts and to evaluate their selective hydrogenation characteristics for the linolenyl ester groups in soybean oil. Also included were binary copper-chromium oxide catalysts, which are extremely selective for linolenate hydrogenation in soybean oil.

TABLE I
Hydrogenation of Soybean Oil with Sodium Borohydride-Reduced Catalysts
(Oil—1 ml; hydrogen pressure—1 atmosphere)

Catalyst	Concn. of metal—wt %	Temp., C	Time, min	Fatty acid composition, %				I.V. (calcd.)	trans, %	Selectivity	
				S	M	D	T			K_{Le}/K_{Lo}	K_{Lo}/K_{01}
		Soybean oil		3.9	26.0	52.5	7.3	132	0	....	....
Ni	10	30	36	7.3	36.7	42.2	3.5	114	6.0	2.5	2.6
Pt/Celite	0.4	25	34	10.1	30.8	43.8	5.2	116	tr	1.5	1.0
Pd[a]/Celite	0.1	25	100	5.5	40.3	40.5	3.7	115	9.2	2.0	7.1
Co/Celite	1–2	175	50	4.3	42.7	39.6	3.4	114	16.9	2.1	40.0
Fe/Celite	2	200	No hydrogenation								
Ag/Celite	2	200	No hydrogenation								

Abbreviations: S, stearate; M, monoene; D, diene; T, triene.
[a] 4 ml soybean oil.

Experimental

Catalysts

The preparation of borohydride-reduced catalysts is exceedingly simple and rapid. First 1 g nickel acetate was dissolved in 50 ml distilled water in a centrifuge tube and then stirred magnetically. While an inert atmosphere of nitrogen was maintained above the solution, about 12 ml of a 1M sodium borohydride solution was added slowly. There was hydrogen evolution while a black precipitate was formed. The supernatant was separated from the precipitate by centrifugation. The catalyst was freed of excess borohydride and other soluble salts by washing with three 50-ml portions of distilled water. This was followed by an absolute alcohol wash and then by an ether wash. The yield of catalyst was always greater than theoretical because of the partial oxidation of the catalyst (16). For maximum activity metal catalysts should be protected from air with an inert atmosphere of nitrogen. Catalysts were similarly prepared from palladium chloride, chloroplatinic acid, cobalt acetate, ferric chloride, silver nitrate, copper nitrate and chromium nitrate. To produce supported catalysts, Celite (Johns-Manville) was added to the metal salt solutions before the addition of borohydride.

Hydrogenations

The glass manometric apparatus used for catalytic reductions has been described previously (11). The powdered catalyst and a magnetic stirring bar were placed in the hydrogenation flask; the system was evacuated and then filled with hydrogen gas at atmospheric pressure. When proper temperature was attained, the system was again evacuated and filled with hydrogen; 1 ml soybean oil was introduced into the flask through the serum cap with a syringe and needle. The magnetic stirrer was started and hydrogenation was continued until a predetermined amount of hydrogen had been taken up. Usually enough hydrogen was added to reduce the iodine value (IV) from 132 to 115; however, with copper-chromium catalysts, which are very selective, hydrogen was added to reduce the IV only to 120. The oil was then separated from the catalysts and converted to the corresponding methyl esters for gas-liquid chromatography (GLC). From the fatty acid composition of the initial and hydrogenated soybean oils, selectivity ratios, that is, the ratios of rates of hydrogenation of linolenyl to linoleyl groups (K_{Le}/K_{Lo}) and linoleyl to oleyl groups (K_{Lo}/K_{01}) were determined with an analog computer assuming consecutive reactions Le (Triene) $\longrightarrow$ Lo (Diene) $\longrightarrow$ 01 (Monoene) (5).

Analytical Methods

Methyl esters were prepared by refluxing 1 ml oil and 10 ml methanol for 1 hr with 0.5% sodium methoxide catalyst. The percentage of isolated *trans* was determined with a Baird Atomic KM-1 instrument by comparing IR absorption of the methyl esters in carbon disulfide solution at 10.36 μ region to that of methyl elaidate. Diene conjugation and per cent linolenate were measured by the AOCS Official Method (1) with a Cary recording spectrophotometer.

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

Results and Discussion

Analyses of soybean oil hydrogenated with sodium borohydride-reduced nickel, platinum, palladium, cobalt, silver and iron are shown in Table I. Iron and silver did not show any activity at 200C even though reports to the contrary appear in the literature (9, 12). All the catalysts lost some activity when exposed to air; nickel completely lost its ability to hydrogenate at room temperature. Platinum had the least tendency for isomerization and was the least selective for linolenate hydrogenation (K_{Le}/K_{Lo}); thus previous findings from this Laboratory were confirmed (11). The low linoleate selectivities (K_{Lo}/K_{01}) observed with nickel, palladium and platinum resulted from the nonselective temperature conditions employed. Linoleate selectivity can be improved by increasing the temperature of hydrogenation.

Nickel catalysts were modified by incorporating various metals up to 2% (Table II). These catalysts were exposed to air during weighing. Since all runs had induction periods, the rates given are the maximum observed during the reaction. With the exception of zirconium, all the metals enhanced activity of the nickel catalyst. No significant differences were observed in selectivities or in *trans* isomer formation.

The results of hydrogenation of soybean oil with copper-chromium catalysts appear in Table III. Copper nitrate was reduced by sodium borohydride to a black precipitate presumably copper oxide. With

TABLE II
Hydrogenation of Soybean Oil with Modified Nickel Catalysts
(Oil—2 ml; temp—140C; concentration of metal 0.1%)

Catalyst	Rate (ml H_2/min/ml oil)	I.V. (calcd.)	trans %	Selectivity	
				K_{Le}/K_{Lo}	K_{Lo}/K_{01}
Ni	0.58	115	10.7	2.1	6.3
Ni-Zr	0.44	116	10.7	1.7	6.1
Ni-Pt	0.88	116	9.9	1.9	7.4
Ni-Pd	0.78	115	9.0	2.2	6.1
Ni-Cu	0.72	116	9.2	1.7	6.5
Ni-Cr	0.82	117	10.1	1.9	10.0

TABLE III

Hydrogenation of Soybean Oil with Copper-Chromium Catalysts
(Sample—1 ml; temp—150C; support—Celite)

Catalyst	Time, min	Fatty acid composition, %			I.V. (calcd.)	% Le (alkali isomerization)	% Conj. diene (UV)	trans, %	Selectivity K_{Le}/K_{Lo}
		M	D	T					
	Soybean oil	26.0	52.5	7.3	132	7.3	....	....	....
Cu 20[a]	130	32.7	47.6	5.1	124	....	....	...	2.5
Cr[b] 20	No hydrogenation								
Cu-Cr 20-0.2	87	35.4	47.1	2.7	119	2.1	tr	8.9	5.0
Cu-Cr 20-1	79	36.0	47.6	1.8	118	0.7	0.9	9.7	6.8
Cu-Cr 20-2	59	35.6	48.8	1.9	120	0.5	1.2	10.7	7.3
Cu-Cr 20-5	79	34.3	49.1	2.8	122	1.5	0.9	8.4	6.1
Cu-Cr[c] 10-10	72	30.5	52.0	4.2	127	3.0	1.0	8.2	7.3
Cu-Cr[d] 20-2	59	35.6	48.0	2.4	120	0.6	1.0	11.5	5.9

[a] Milligrams metal. [b] No support. [c] Temp, 160C. [d] Chromium chloride was used instead of chromium nitrate.

it, the soybean oil hydrogenated slowly, and after partial reduction all the catalyst turned red and became inactive. This reaction is an indication of the formation of either monovalent or metallic copper (6). Chromium nitrate was reduced to a bluish-green gel-like precipitate, which probably is similar to the chromium oxide gel described by Burwell et al. (4). It showed no activity for hydrogenation even when the temperature was raised to 200C. When both copper and chromium salts were reduced together, moderately active catalysts were obtained and were much more selective than the copper catalysts alone. Also, addition of chromium stabilized the copper catalyst since no color transformation was observed in the catalysts that contained more than 1% chromium (metal basis). Evidently 1% chromium seems barely sufficient to protect the copper catalyst, for at the end of hydrogenation the catalyst had a somewhat reddish color. Maximum selectivity and best activity were observed with catalysts that contained 5 to 10% chromium. No increase in saturated acids was observed with copper-chromium catalysts; thus the linoleate selectivity (K_{Lo}/K_{01}) was very high and was greater than any other catalysts we have tested.

Ultraviolet spectrophotometric analyses showed that about 1% conjugation is produced during hydrogenation. When conjugation is present, it was noted that the triene values obtained by GLC were always higher than the per cent linolenate values obtained by alkali isomerization. This discrepancy results because in GLC one of the conjugated diene isomers (*cis,trans*) has the same retention time as linolenate. Hence the triene values given in Table III also include some conjugated diene. Our reported selectivity ratios were obtained from GLC data, and if the alkali-isomerization values for linolenate are considered, the selectivity ratios for copper-chromium catalysts will be much higher. For example, both the catalysts containing 10% chromium will have a selectivity ratio of 14.

TABLE IV

Hydrogenation of Soybean Oil with Modified Copper-Chromium Catalysts
(Sample—1 ml; temp—150C; support—Celite)

Catalyst	Time, min	I.V. (calcd.)	trans, %	Selectivity K_{Le}/K_{Lo}
Cu-Cr-Ni 20-2-0.6	28	112	17.0	1.9
Cu-Cr-Ni 20-5-0.5	47	113	17.4	2.6
Cu-Cr-Ni 20-10-0.4	82	116	15.4	3.2

Except for the boron present in sodium borohydride-reduced copper (15), it is not known whether these copper-chromium catalysts differ from catalysts prepared by precipitation methods (6). However, we have observed that a commercial sample was devoid of activity at 150C for the hydrogenation of soybean oil and that it became active upon treatment with sodium borohydride. This procedure may also well afford a novel method of activating spent catalysts.

The effect of incorporating nickel into copper-chromium catalysts is shown in Table IV. Apparently, addition of nickel decreased the selectivity for linolenate hydrogenation and increased the *trans* isomer formation despite increased activity of the catalysts as evidenced by reduced times of hydrogenation.

The development of certain undesirable flavors in soybean oil has been attributed to linolenate groups (8). Soybean oil with improved stability can therefore be produced if linolenate can be eliminated. Of the catalysts studied, the copper-chromium seem most promising for selectively hydrogenating linolenate. Copper-chromium catalysts are not new (6) and are used commonly to produce fatty alcohols from esters, to reduce polyunsaturates in fish oils and, more recently, to hydrogenate soybean oil (14). Since publication of our abstract (13) on sodium borohydride-reduced copper-chromium catalysts, a report (7) disclosing similar high selectivities with a copper-on-guhr catalyst appeared.

Trace amounts of copper remaining in the oil are deleterious. If copper can be removed entirely from the oil, then copper-chromium catalysts may be useful to produce a more stable salad oil from soybean oil.

Regardless of the practicality of these copper-chromium catalysts, the discovery of their high selectivities for linolenate does encourage further studies of mixtures of catalytic and noncatalytic metals, particularly those metals which may not have the prooxidant disadvantages of copper. The borohydride procedure of preparing catalysts with mixtures of metals will greatly facilitate the conduct of such research.

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Determination of Aflatoxins in Individual Peanuts and Peanut Sections[1]

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Abstract

Subsamples of a given lot of peanuts may vary greatly in aflatoxin content due to extreme variability in the degree of contamination of individual kernels. A micro method, adapted from the aqueous acetone procedure recently proposed by Pons and Goldblatt for the determination of aflatoxins in cottonseed products, was developed to permit accurate determination of aflatoxins in individual kernels and kernel sections.

Use of this procedure permitted the topographic distribution of aflatoxins within single kernels to be mapped and indicated that the toxins are not uniformly distributed within contaminated kernels, even when the kernel contains a high level of aflatoxins. Although wrinkling or discoloration sometimes indicated that a kernel was contaminated, this type of physical damage was not found to be a reliable indication of aflatoxin content. Also it was noted that a few apparently sound and mature kernels contained high levels of aflatoxins.

Introduction

STRAINS OF THE COMMON MOLD *Aspergillus flavus* have been found to produce highly toxic metabolites recently named aflatoxins (1). These aflatoxins have been designated B_1, B_2, G_1, and G_2, the letters indicating that 2 fluoresce blue and 2 green under ultraviolet light, and the subscripts identifying their relative mobility under specific conditions of chromatography.

Although the toxins are not limited to peanuts (2,3) this commodity was the first to be implicated and is one of the commodities most seriously threatened in the United States since such a large portion is consumed as food. As numerous samples of peanuts were analyzed for aflatoxins at this laboratory, it became evident that sampling would be a major problem: it appeared that a few highly contaminated kernels unevenly distributed among a large number of uncontaminated ones caused large differences among assays of subsamples. To identify the contaminated kernels and also to determine the distribution of aflatoxin within the kernel, it was necessary to devise a method for assaying individual peanuts or parts of peanuts.

Most of the current methods involve Soxhlet extraction (4), large column (5), or phasic separations (6). The aqueous acetone method originally developed by Pons and Goldblatt for the determination of aflatoxins in cottonseed (7) is, however, particularly adaptable to micro techniques. Because it extracts only negligible amounts of oil while readily dissolving aflatoxins, this solvent is especially useful for examination of individual peanuts and peanut sections weighing as little as half a milligram. The amount of sample necessary is inversely related to the parts per billion aflatoxins. For example, on a sample weighing 400 mg it is possible to estimate aflatoxins in concentrations as low as 24 ppb; on the other hand, if the level of toxin is high enough, samples weighing as little as 0.3 mg can be assayed accurately.

Procedure and Results

Method for Assay of Aflatoxins

Whole peanuts or peanut sections are weighed and then comminuted into fine particles (0.5 to 1 mm) with a sharp razor blade without the expression of oil. The sample is allowed to soak for 30 min in 5 ml of 70% acetone in a 15 ml graduated conical tipped centrifuge tube and is stirred at intervals to ensure maximum extraction. Two ml of 20% lead acetate is then added, the mixture stirred, and 6 ml of distilled water added. The sample is centrifuged for 10 min at 4000–5000 rpm in an angle head centrifuge. The supernatant is quantitatively decanted into a 60 ml separatory funnel. The amount of 5 ml of 70% acetone is added to the residue, and the mixture is stirred and allowed to stand for 30 min. After 8 ml of distilled water is added, the mixture is recentrifuged for 5 min; the centrifugate from this extraction is added to that in the separatory funnel. This combined centrifugate is then shaken in the separatory funnel with 2 separate 20 ml portions of chloroform. After the lower chloroform layer has separated, it is filtered through about 25 g of anhydrous sodium sulfate into a 50 ml beaker. The bed of sodium sulfate can be conveniently prepared by inserting a plug of glass wool into the constriction of a drying tube (1.4 x 10 cm). After most of the

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