&Supported Gold Catalysis in the Hydrogenation of Canola Oil

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ABSTRACT

The catalytic activity of gold supported on silica or γ-alumina has been studied in the hydrogenation of canola oil. In the hydrogenation of butadiene and pentene using these catalysts, high stability, low yield of trans-isomers and high monoene selectivity have been reported in the literature.

Catalysts containing 1% and 5% Au w/w on porous silica and γ-alumina were active in hydrogenating canola oil in the range of 150 to 250 C and 3550 to 5620 kPa. The activity level of these catalysts was about 30 times lower than that shown by the standard AOCS Ni catalyst based on the concentration of metal (g Au/L oil). Up to 91% monoene content was obtained using these catalysts in comparison with a maximum of 73% for the AOCS standard Ni catalysts. Gold catalysts can be recovered easily by filtration and reused several times without a decrease in activity. The hydrogenated oil was nearly colorless. No gold was detectable in the oil. Contrary to claims in the patent literature, the gold catalyst produces higher concentrations of trans-isomers than does nickel. However, using gold catalysts the complete reduction of linolenic acid in canola oil can be achieved at a lower trans-isomer content in the products than that obtained by using the AOCS standard nickel catalyst.

INTRODUCTION

The low catalytic activity of gold is due mainly to its inability to chemisorb simple molecules such as oxygen and hydrogen. This lack of reactivity is believed to be due to the absence of a partially filled d-band at temperatures below 200 C. Thus, for example, Au neither absorbs dissociatively molecular hydrogen nor catalyzes hydrogenation reactions below 200 C significantly (1), unless supplied with hydrogen atoms or protons from an external source such as the catalyst support. This has been demonstrated in the case of the hydrogenation of 1-butene (2) and ethylene (3).

In several reports (4-6), it has been shown that in the reactions of unsaturated hydrocarbons using supported Group VIII metal catalysts the support plays an important role in determining the catalytic behavior. In particular, the provision of hydrogen to adsorbed species on the metal surface has been discussed.

Hydrogenation of 1,3-butadiene over alumina-supported gold at 200 C has been reported by Buchanan (7). Gold was supported on porous alumina by impregnation of the support with $HAuCl_4$ in solution. The reaction was completely selective for the formation of butene; no butane was ever observed as a reaction product, and the reaction ceased at a pressure drop corresponding to the uptake of 1 mole of hydrogen per mole of 1,3-butadiene.

Hydrogenation of pentene over gold supported on silica or alumina was reported by Sermon and Bond (8). Gold catalysts were prepared using a technique similar to the one mentioned above. The severity of the conditions required to effect the decomposition of the $HAuCl_4$ to metallic gold on the support decreased, and the activity per unit weight of metal in the hydrogenation of 1-pentene at 100 C increased as the concentration of gold decreased from 5.0 to 0.01% by weight. Catalysts containing 5% gold were the only ones to catalyze the isomerization of 1-pentene to 2-pentene simultaneously with hydrogenation to pentane. Catalysts with lower concentrations of gold were effective only in bringing about hydrogenation. No isomeric products (i.e., cis- or trans-2-pentene) were formed. This separation of isomerization and hydrogenation activity has not been observed with any other transition-metal catalyst.

The above mentioned papers culminated in two patents (9,10) on the preparation of gold catalysts supported on porous silica or alumina. These patents claim a zero yield of saturates in the hydrogenation of 1,3-butadiene and no isomerization in the hydrogenation of 1-pentene using gold catalysts. The patents also claim that in the hydrogenation of glyceride oils the products are low in trans-isomer, but no examples are given. This claim is repeated in the review by Gray and Russell (11).

Gold on silica has been shown to be dispersed forming small islands with evidence of Au-Si bonding forming on the SiO_x layer beneath the contact point of the gold particles (12). The average size of gold particles supported on porous silica or alumina has been estimated by transmission electron microscopy and X-ray line broadening to be 3 to 100 nm in size. No correlation has been found between the catalytic activity of silica- and alumina-supported gold catalysts and the degree of dispersion or particle size of the gold (8).

The Ad Hoc Committee on the Composition of Special Margarine (13) called for more research on the effect of trans-isomers of fatty acids in the human diet and encouraged the development of hydrogenation processes that resulted in lower trans-isomer concentrations in partially hydrogenated edible oil products. The nutritional effects of partially hydrogenated soy oil and their relationships to trans-isomer content were reviewed by Applewhite (18).

The objective of the present work was to verify the suitability of gold catalysts for the hydrogenation of edible oils to produce products low in trans-fatty acids, as suggested in the above-mentioned patents.

No reports have been found in the literature regarding the hydrogenation of edible oils using gold catalysts. In the present study, several runs were made using silica- and alumina-supported gold covering a wide range of conditions of temperature, pressure and gold concentration. The dependence of activity, trans-isomer formation and product composition on hydrogenation conditions and the reusability of gold catalysts were studied.

EXPERIMENTAL

Materials

Refined and bleached canola oil (rapeseed oil low in erucic acid) was supplied by Canada Packers Ltd. of Toronto, Ontario.

$HAuCl_4$ was purchased from Johnson Matthey Ltd. Activated silica powder (grade 62, 60-200 mesh), and activated alumina powder (neutral type, 150-135 mesh), were obtained from the Aldrich Chemical Company. The alumina was present in the gamma (γ) form.

Gold Catalyst Preparation

Catalysts containing predetermined quantities of gold on silica and alumina were prepared using basically the method given in British patents 1,472,061 and 1,472,062. $HAuCl_4$ was deposited in the pores of the dry support by impregnating it with an aqueous solution of $HAuCl$. Just enough solution was added to wet the surface of the solid, indicating that pores are filled with solution. The solution concentration was adjusted to yield catalysts containing 0.01, 0.25, 1, 3 and 5% gold by weight. After air-drying the solid to

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make the catalysts free-flowing, the samples were heated in vacuo. The samples containing 0.01 and 0.25% of gold decomposed to metallic gold during this stage. Samples with 1, 3 and 5% gold on the support were reduced in a continuous flow of hydrogen at atmospheric pressure to metallic gold. Some batches were reduced at high hydrogen pressure in a 1-l Parr reactor, or using a 90% hydrazine solution (14). In order to find the optimum conditions for the preparation of gold catalysts, different batches were prepared by varying the time and temperature in all preparation steps. When the reaction was carried out at low hydrogen pressure, the catalyst activity was reproducible and the catalysts were stable. Thus, drying time in air was varied between 0 and 2 days, the drying time in vacuo was varied between 0 and 6 hrs in the temperature range of 100-450 C, and the reaction times were varied between 10 min and 24 hr in the temperature range of 100-450 C.

Hydrogenation Procedure

The oil was rebleached using 0.5% w/w of bleaching clay under a nitrogen atmosphere with continuous agitation at room temperature for 1 hr.

Hydrogenations were carried out in a batch-type Parr reactor, using a 300 ml bomb with agitation fixed at 900 rpm. A charge of 100 g of oil was introduced into the reactor and was warmed up under nitrogen. The time of hydrogen introduction into the reactor was defined as the start of the reaction.

The hydrogenation reaction was monitored by measuring the refractive index of small oil samples obtained periodically throughout the run. Subsequently, iodine values (IV) also were determined.

After hydrogenation, the catalyst was removed from the oil by filtration using Whatman #41 filter paper. The recovered catalyst was washed with chloroform to remove any residual oil.

Catalyst reusability was studied by doing several consecutive hydrogenation runs using the recovered catalyst. Each run was done for 1 hr at 200 C and 3550 kPa. Since it was impossible to avoid catalyst losses during the handling of the products, the oil-to-catalyst ratio was kept constant from one run to another by appropriately decreasing the oil charge in the reactor.

Analytical Methods

Analyses of all hydrogenated oils were performed according to official methods of the American Oil Chemists' Society (15). IV's were determined by the Wijs method (AOCS Cd 1-2 s). Wijs solution (N/5) was purchased from BDH Chemicals, Toronto, Canada. Trans-fatty acids were determined by the infrared spectrophotometric method (AOCS Cd 14-61 with elaidic acid as a standard) using a Perkin-Elmer I.R. 598 spectrophotometer. Fatty acid composition was determined by gas chromatography (AOCS Ce 62, Ce 2-66), using a Hewlett Packard Model 5840A gas chromatograph with a glass capillary column coated with cyanopropyl silicone and operated isothermally at 185 C. A flame ionization detector was used for quantitation.

The metal content in the oil and on the support was determined by neutron activation analysis using the SLOW-POKE reactor facility at the University of Toronto.

RESULTS AND DISCUSSION

As the minimum gold concentration at which reasonable hydrogenation activity was observed was 0.9 g Au/L at 200 C and 3550 kPa, it is not practical to use catalysts containing less than 1% gold w/w for hydrogenation of canola oil. Thus, in run 2, Table II, using 1% Au/Al$_2$O$_3$ the quan-

TABLE I

Preparation of Gold Catalyst

Batch catalyst		Drying		Reduction		Activity[c]
#	% Au/supp. w/w	Temp. (C)	Time (min)	Temp. (C)	Time (min)	100 Δ IV/min/ (g Au/l oil)
1	5.0	–	–	300	120	4.3
2	5.0	–	–	300	120	3.6
3	5.0	100	60	250	120	1.7
4	5.0	250	20	350	20	4.2
5	5.0	200	20	300	20	5.3
6	5.0	300	10	450	2	3.0
7	5.0	300	20	300	5	1.4
8	3.0	100	60	200	60	3.5
9	3.0	260	60	300	10	4.1
10	3.0	325	20	375	30	8.2
11	3.0	375	30	375	20	2.9
12	3.0	200	30	375	20	4.4
13	3.0	350	120	400	10	4.2
14[a]	5.0	–	–	300	120	24.2
15[a]	5.0	–	–	300	120	2.5
16[a]	5.0	–	–	300	120	7.0
17[a]	5.0	–	–	300	120	0.0
18[a]	3.0	–	–	300	24 hr	0.5
19[b]	5.0	–	–	35	360	0.7
20[b]	5.0	200	60	35	360	1.5

[a]Catalysts reduced at 3550 kPa in a batch reactor.
[b]Catalysts reduced using hydrazine.
[c]At 200 C, 3550 kPa.
The size of each batch ranged from 11.8 to 30 g, except batches 2 and 17 which were 100 and 120 g, respectively.
In batches 6, 7 and 13, the support was dried in vacuo at 400 C for 60 min.

tity of catalyst used was 10% w/w of oil. Alumina was found to produce more stable gold catalysts than silica. This also was observed by Sermon and Bond (16) in the hydrogenation of pentene using silica-supported gold catalyst. In their study the activity of this catalyst declined slowly until it reached a constant value. This decline in activity was not observed when γ-alumina was used as the support.

Accordingly, in the present study only those catalysts containing more than 1% gold on alumina were studied in detail. The activity of 20 batches of gold catalyst prepared under varying conditions are presented in Table I.

The activity varied among different batches in which different conditions for the preparation of the catalyst were used, but consistent trends could not be determined (Table I). The highest catalytic activity was obtained when high-pressure hydrogen was used for the reduction (Batch #14). Unfortunately, using this method the catalytic activity was not reproducible. In the case of reduction with hydrazine, very low activity was observed. All gold catalysts were red or dark blue in color after reduction, indicating metallic gold of colloidal size (8). The activity of catalysts obtained by reduction at low hydrogen pressure was more reproducible and stable; after reusing the 5% Au/Al$_2$O$_3$ several times there was no gold detachment from the support, and a progressive but uneven increase in catalytic activity was observed (Fig. 1). This suggests that the gold was not completely reduced and the reduction process continued during hydrogenation. No fresh catalyst prepared by any of the methods of preparation reached the activity of the catalyst reused up to 20 times. Batches A and B in Figure 1 were chosen to represent maximum and minimum activity in the gold catalyst from a total of 13 batches reduced at low hydrogen pressure (Table I, batches 10 and 7). Although the evidence seems to indicate that further reduction is necessary to obtain higher activity, no increase in activity was observed with increasing reduction times in the preparation of the gold catalysts.

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TABLE II

Influence of Temperature, Pressure and Gold Concentration on Hydrogenation Activity and Isomerization Index Using Catalysts Prepared at Low Hydrogen Pressure

| Run[a] | T (C) | P (kPa) | Gold concentration | | | Specific activity | Specific isomerization index |
			on support (% w/w)	in oil (g Au/l)	Support	100 Δ IV/min/ (g Au/l oil)	Δ % trans/ Δ IV
1	200	3550	1	0.91	SiO_2	3.5	0.52
2	200	3550	1	0.91	Al_2O_3	4.1	0.84
3	200	3550	5	2.40	Al_2O_3	4.0	0.90
4	200	5620	5	2.40	Al_2O_3	8.8	0.89
5	150	5620	5	4.50	Al_2O_3	0.4	1.00
6	200	1830	5	4.50	Al_2O_3	1.1	0.88
7	200	3550	5	4.50	Al_2O_3	2.4	1.33
8	200	5620	5	4.50	Al_2O_3	6.2	1.16
9	250	1830	5	4.50	Al_2O_3	9.6	0.96
10	250	5620	5	4.50	Al_2O_3	12.2	1.27
11	150	5620	5	9.10	Al_2O_3	0.2	1.38
12	200	1830	5	9.10	Al_2O_3	2.7	1.38
13	200	5620	5	9.10	Al_2O_3	3.8	0.96
14	250	1830	5	9.10	Al_2O_3	5.8	1.10
15	250	5620	5	9.10	Al_2O_3	8.2	1.07

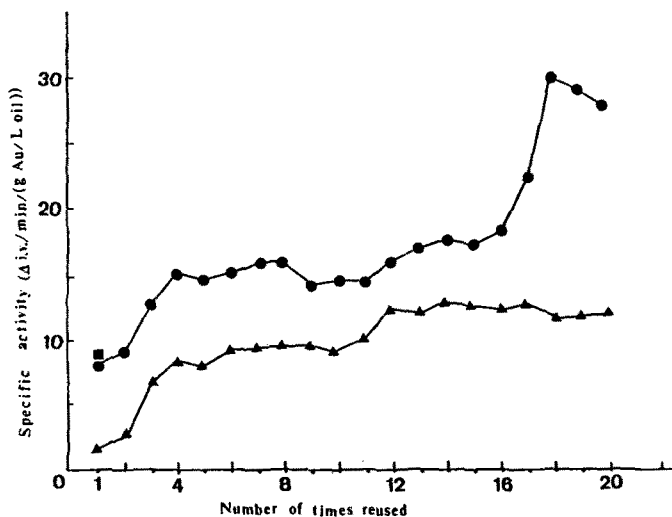[a]Runs 3 to 15 were done using the same batch of catalyst.

FIG. 1. Reusability of different batches of 5% Au/Al_2O_3 catalysts reduced at low hydrogen pressure. • = batch A; ▲ = batch B, and ■ = batch B (ground). Hydrogenation conditions: 200 C, 3550 kPa, 4.5 g Au/l oil.

TABLE III

Specific Activity Dependence on Temperature, Pressure and Gold Concentration

| Temperature (C) | 200 | 200 | 250 | 250 |
Pressure (kPa)	1830	5620	1830	5620
Metal concentration (g Au/l oil)	Specific activity[a]			
4.5	1.1	6.2	9.6	12.2
9.1	2.7	3.8	5.8	8.2

[a]Specific activity expressed in 100 Δ IV/min/(g Au/l oil); data were selected from Table II.

The presence of metallic gold on alumina was confirmed by X-ray powder diffraction in all analyzed samples containing 1 and 5% Au. In catalyst samples where significant gold detachment was detected, the detached gold particles were big enough to become trapped in the filter paper

because no gold was detected in any of the oil samples. It is important to note that in all cases when the catalyst samples were reduced under continuous hydrogen flow, gold detachment was negligible.

The increase in catalytic activity of the gold catalysts also can be explained in terms of gradual particle-size reduction occurring during reuse, resulting in increased surface area and improved diffusion to the active sites during hydrogenation. This was demonstrated clearly using freshly ground catalyst. The higher activity was equivalent to that obtained after 4 reuses of the catalyst from the same batch without grinding (Fig. 1). The gradual increase in activity observed on reusing gold catalysts may, in fact, be due to a combined effect of further reduction and decrease in the particle size of the support.

The variation of activity of the gold catalyst with temperature, hydrogen pressure and gold concentration was studied in a series of runs using a single batch of catalyst (Table II). In the range of conditions studied, an increase in any of the variables resulted in an increase in hydrogenation activity, expressed as the average decrease in IV during the first 60 min of the run. This is seen in Table III, in which the changes in activity for two levels of temperature, pressure and gold concentration are shown clearly (values taken from Table II). It is important to note that at either of the two levels of temperature (200 and 250 C) there is a significant influence of the pressure (3550 and 5620 kPa) on the activity. This supports the explanation given above for the increased activity observed using ground 5% Au/Al_2O_3 catalyst (Fig. 1). This evidence suggests a significant resistance to hydrogen mass transfer through the pores of the alumina. To maintain the proper concentration of hydrogen required to complete the hydrogenation of unsaturated compounds, sufficient pressure should be used. On the other hand, the drop in specific activity at higher concentration observed in Table III suggests that a further increase of pressure beyond 5620 kPa could result in increased specific activities at the higher metal concentration.

The trans-isomer content of the hydrogenated oils, represented by the average change in trans-isomer content per unit of IV during the first 60 min (Specific Isomerization Index), remained at high values under all conditions (Table II). The maximum trans-isomer content obtained using gold catalysts is even higher than for the AOCS standard Ni catalyst (Tables IV, VII).

TABLE IV

Fatty Acid Composition of Hydrogenated Canola Oil Using 5% Au/Al$_2$O$_3$ Catalyst[a]

Time (hr)	IV	% trans	C16:0 %	C18:0 %	C18:1 %	C18:2 %	C18:3 %	C20:0 %
0.00	117.0	0.0	4.1	1.7	60.1	22.7	10.5	0.8
0.25	103.4	8.8	3.4	1.9	71.8	19.3	2.7	0.7
0.50	92.4	24.2	3.5	2.4	86.0	7.1	—	0.9
0.66	86.8	34.8	3.6	3.7	88.7	3.0	—	0.8
0.92	83.1	43.6	3.4	5.0	90.6	—	—	0.8
1.25	81.2	51.1	3.7	7.1	88.3	—	—	0.8
2.00	75.4	58.4	3.6	10.8	84.7	—	—	0.8
3.00	70.1	57.6	3.8	17.6	77.8	—	—	0.7

[a]Catalyst from batch #14 (Table I) with conditions: T = 200 C; P = 3500 kPa; 2.3 g Au/l oil.

TABLE V

Fatty Acid Composition of Hydrogenated Canola Oil Using 1% Au/Al$_2$O$_3$ Catalysts[a]

Time (hr)	IV	% trans	C16:0 %	C18:0 %	C18:1 %	C18:2 %	C18:3 %	C20:0 %
0.00	117.0	0.0	3.7	1.4	58.5	24.7	10.7	0.8
0.25	116.0	0.8	3.9	1.4	58.8	25.6	8.6	0.7
0.50	114.7	2.0	3.9	1.5	60.2	27.1	6.6	0.5
0.75	111.1	4.4	3.7	2.0	63.1	25.5	5.2	0.5
1.00	107.5	6.8	3.8	2.2	64.7	24.8	4.0	0.4
1.50	102.6	15.6	3.4	2.3	68.0	22.8	3.0	0.4
2.00	98.4	19.7	3.6	4.3	72.6	18.3	0.6	0.5

[a]Catalyst from batch #8 (Table I) with conditions: T = 200 C; P = 3550 kPa; 4.5 g Au/l oil.

TABLE VI

Reusability of 1% Au/Al$_2$O$_3$ in Hydrogenation of Canola Oil[a]

| Time (hr)	IV	% trans	Fatty acid composition C16:0 %	C18:0 %	C18:1 %	C18:2 %	C18:3 %	C20:0 %
First run								
0.25	115.4	0.3	3.9	1.3	60.4	25.0	8.0	0.8
1.00	114.8	0.3	3.9	1.4	61.3	24.9	7.5	0.8
2.00	113.3	1.8	4.0	1.1	63.5	25.0	5.4	0.8
3.00	110.4	3.5	3.9	1.8	63.7	23.8	5.6	0.9
4.00	108.9	5.6	3.9	1.8	67.3	21.5	4.4	0.9
5.00	106.4	8.1	3.9	1.9	68.3	21.7	3.1	1.0
6.00	103.5	10.8	4.0	1.5	73.4	19.0	1.1	0.9
Second run								
6.00	101.4	11.4	4.1	1.5	75.7	16.8	0.7	1.0
Third run								
6.00	100.6	10.9	3.9	1.7	74.4	18.2	0.7	1.0
7.00	97.7	14.6	3.9	2.0	77.0	15.7	0.2	1.0
Fourth run								
6.00	99.1	13.5	4.2	1.8	75.0	16.3	1.4	1.0
Fifth run								
6.00	98.6	15.9	3.6	1.8	79.9	13.5	0.1	0.9
9.00	87.7	28.7	4.0	2.4	86.9	5.6	0.3	0.7
Sixth run								
6.00	94.8	25.3	3.8	2.1	80.3	12.5	0.3	0.9
9.00	88.9	29.7	3.9	2.4	86.9	5.8	0.2	0.7

[a]Conditions: T = 200 C; P = 3550 kPa; 0.91 g Au/Al$_2$O$_3$.
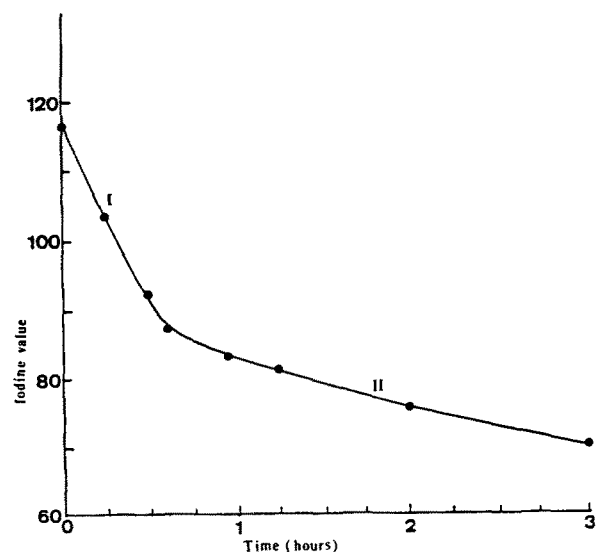
FIG. 2. Change in iodine value during hydrogenation of canola oil catalyzed by 5% Au/Al$_2$O$_3$ catalysts (200 C, 3550 kPa).

TABLE VII

Hydrogenation of Canola Oil over AOCS Standard Ni Catalyst

Time (hr)	IV	% trans	C16:0 %	C18:0 %	C18:1 %	C18:2 %	C18:3 %	C20:0 %
Run 1[a]								
0.25	110.1	8.1	4.0	2.6	63.0	22.0	5.4	0.8
0.50	104.9	20.8	4.4	4.1	66.6	18.4	2.7	0.7
1.25	75.7	45.4	4.4	17.3	72.7	2.5	—	—
1.75	63.1	45.1	4.4	25.5	66.6	2.1	—	—
2.00	60.1	46.2	5.0	30.0	64.2	0.6	—	—
Run 2[b]								
0.25	113.9	1.6	4.3	1.8	61.6	23.9	7.1	1.2
0.50	112.6	2.4	4.0	1.9	61.6	24.1	6.9	1.2
1.00	108.4	5.7	4.1	1.9	62.6	24.0	6.4	0.9
1.50	105.5	8.3	4.3	2.2	64.4	22.3	5.9	0.8
2.00	103.3	11.0	4.3	2.3	65.3	22.1	4.9	0.8
3.00	99.6	21.6	3.9	3.0	68.5	20.5	3.2	0.8
4.00	96.5	30.7	4.0	3.6	71.2	18.1	2.1	0.8

[a]Conditions: T = 180 C; P = 790 kPa; 1.0 g Ni/l oil.
[b]Conditions: T = 180 C; P = 790 kPa; 0.16 Ni/l oil.

The change of the IV with time (Fig. 2 and Tables IV, V and VI) clearly shows two distinct regions with different hydrogenation rates. In the first region (Fig. 2, I) dienes and trienes are hydrogenated faster than monoenes, giving rise to a large increase in monoene content (maximum 91%). In the second region (II) the observed overall rate is determined predominantly by the rate of reduction of the monoenes. This high selectivity for monoene formation during hydrogenation of canola oil agrees with the findings reported by Buchanan and Webb (7) for the hydrogenation of butadiene, where a high yield of butene was obtained. The product distribution remained unchanged after the gold catalysts were reused several times (Table VI). Probably a mechanism similar to that suggested by Buchanan and Webb is applicable to the hydrogenation of canola oil.

In spite of the high trans-isomer formation, gold catalysts could be useful in the partial hydrogenation of edible oil to increase oxidative stability; significant reduction of linolenic

acid can be achieved at lower levels of trans-isomer and stearic acid content (Tables IV, V and VI) than that when the AOCS nickel catalyst is used (Table VII). Thus, for example, hydrogenated oil containing 2.7% linolenic acid, 103.4 IV and 8.8% trans-isomer content was obtained with gold catalyst in comparison with 4.9% linolenic acid, 103.3 IV and 11% trans-isomer content using a standard Ni catalyst (Tables IV and VII). This is an important conclusion. In addition, gold catalysts produced nearly colorless oil free of traces of gold. In fact, a decrease in color from 1 red, 20 yellow to 1 red, 7 yellow was observed as a result of hydrogenating canola oil (Method Ce 13b-45 [15] using a 133.33 mm [5¼"] cell). This color reduction occurs very early in the reaction (at very low hydrogenation levels), probably due to the rapid hydrogenation of pigments.

The catalyst activity and selectivity of the gold catalysts as well as the product characteristics are unaffected by the reuse of the catalyst (Table VI). Furthermore, the catalyst's high stability and easy separation from the oil suggest that it may be suitable for use in a continuous hydrogenation system such as that described by Koritala et al. (17). Multiple reuse could offset the high initial cost of these catalysts. Supported gold catalysts may be suitable for the stabilization of high-linolenic oils by the rapid reduction of linolenic acid, thus producing oils with greatly improved stability toward oxidation, polymerization and flavor reversion. This may give frying fats of excellent quality.

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♣Kernel Oils of Seven Plant Species of Zaire

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ABSTRACT

Kernels of *Pentaclethra macrophylla, Allanblackia floribunda, Panda oleosa, Treculoa africana, Desplatzia dewevrei, Garcinia kola* and *Milletia laurentii* were found to contain respectively 45.9, 67.6, 50.5, 11.8, 20.4, 2.1 and 22.9% oil (% dry matter). Gas liquid chromatography showed the major fatty acids of the kernel oils were as follows: *P. macrophylla*, 18:1 (31.3%) and 18:2 (40.4%); *A. floribunda*, 18:0 (55.9%) and 18:1 (43.3%); *P. oleosa*, 16:0 (32.0%), 18:1 (30.2%) and 18:2 (29.2%); *T. africana*, 16:0 (25.7%), 18:1 (32.7%) and 18:2 (25.8%); *D. dewevrei*, 16:0 (37.8%), 18:1 (18.1%) and 18:2 (35.0%); *G. kola*, 16:0 (19.0%), 18:1 (38.4%) and 18:2 (23.7%), and *M. laurentii*, 18:1 (44.9%) and 18:2 (17.6%).

INTRODUCTION

The palm tree, *Elaeis guineensis*, and the groundnut, *Arachis hypogaea*, are the most important sources of edible and commercial oils in Zaire. However, the oils of many wild plants have a potential economic value. Kernels of some wild plants from Zaire have been analyzed for oil content, fatty acid composition and characteristics by Adriaens (1, 2), Kabele Ngiefu (3, 4, 5), Vieux (6, 7), Meara (8) and Hilditch (9).

In the work reported here, kernel oils of 7 plant species were extracted and their fatty acid compositions determined in order to select the species with the best commercial value. The following species were analyzed: *Pentaclethra macrophylla* (Mimosaceae); *Allanblackia floribunda* (Guttiferaceae); *Panda oleosa* (Pandaceae); *Treculia africana* (Moraceae); *Desplatzia dewevrei* (Tiliaceae); *Garcinia kola* (Guttiferaceae) and *Milletia laurentii* (Papilionaceae). These plants, which grow wild in Yangambi (Zaire), were recommended by the National Institute of Agricultural Research (Yangambi, Zaire).

MATERIALS AND METHODS

The dried, finely ground kernels were extracted quantitatively with petroleum ether (b.p. 40–60 C) in a Soxhlet apparatus. The lipids, extracted with a mixture of chloroform:methanol (2:1, v/v) as described by Folch (10), were fractionated by thin-layer chromatography (TLC) on silica gel G using as a solvent system petroleum ether (b.p. 40–60 C):ethyl ether:acetic acid (80:20:1, v/v/v) (11). Lipid components were identified by co-chromatography with pure compounds and by comparison of their Rf values. Lipids appeared under ultra-violet light with a 0.0012% solution of Rhodamine 6G (12). Fatty acid methyl esters were prepared with a mixture of H_2SO_4:methanol:benzene (0.06:2:1, v/v/v) at 70 C for 2 hr (13). Methyl esters were separated on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and stainless steel columns. The columns were packed with 10% diethyleneglycol succinate (DEGS) on 80–100 mesh chromosorb W. Nitrogen was used as a carrier gas. The peak areas were measured by the triangulation method and were identified by comparing their retention times with those of a known standard.

RESULTS AND DISCUSSION

The results are summarized in Table I.

The oil content varies from 2.1% in *Garcinia kola* to 67.6% in *Allanblackia floribunda*.

The low lipid content of *Garcinia kola* eliminates its value as a lipid source. On the other hand, kernel oils of *Panda oleosa, Treculia africana* and *Desplatzia dewevrei* could be used as edible oil sources because of their relatively high percentage of unsaturated fatty acids, in par-