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Comparison of Acidic and Basic Volatile Compounds of Cocoa Butters from Roasted and Unroasted Cocoa Beans

James T. Carlin[1], Ken N. Lee[2], Oliver A.-L. Hsieh[3], Lucy Sun Hwang[4], Chi-Tang Ho and **Stephen S. Chang***
Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903

A total of nine acidic and 83 basic compounds was identified in the roasted and unroasted cocoa butter samples. Forty seven of the compounds identified are being reported for the first time in cocoa. The higher concentration of short chain fatty acids in the unroasted cocoa butter is responsible for its acidic aroma characteristics. The roasted cocoa butter generally contained greater numbers and higher concentrations of compounds whose formations would be favored by thermal processing. These compounds included pyrazines, thiazoles, oxazoles and pyridines. The aromas of many of these compounds are characteristic of the aroma differences between the two cocoa butters and contribute to the cocoa aroma of roasted cocoa butter.

The price and popularity of cocoa have made it one of the most studied natural flavors. More than 400 volatile flavor compounds have been identified as constituents of cocoa. The majority of research on cocoa has dealt with cocoa beans, cocoa powder, cocoa liquor and chocolate as sources of flavor. Only three publications exist which investigate cocoa butter as a source of flavor.

Van Elzakker and van Zutphen (1) identified 23 volatile flavor compounds in the neutral and basic fractions of a vacuum steam distillate of cocoa butter. Rizzi (2) identified nine alkylpyrazines in the basic fraction of a vacuum steam distillate of cocoa butter. Rostagno et al. (3) identified 30 volatile flavor compounds in a steam distillate of cocoa butter and developed an analytical method to evaluate the aroma intensity of different varieties of cocoa butter.

*To whom correspondence should be addressed.
[1]Present address, Thomas J. Lipton, Inc., Englewood Cliffs, NJ.
[2]Present address, Oscar Meyer, Inc., Madison, WI.
[3]Present address, Campbell Soup Company, Camden, NJ.
[4]Present address, Graduate Institute of Food Science & Technology, National Taiwan University, Taipei, Taiwan, Republic of China.

The flavor of cocoa butter depends on the processing conditions to which the cocoa beans are subjected. Cocoa butter obtained from roasted cocoa beans has a strong flavor reminiscent of cocoa. Cocoa butter obtained from unroasted cocoa beans which have been given a steam treatment has a considerably milder, yet distinctive, flavor.

The objective of this study was to isolate, identify and semiquantitate the volatile flavor compounds of cocoa butters obtained from roasted and unroasted cocoa beans. This paper reports the isolation methodology employed and the acidic and basic compounds identified. The neutral compounds identified will be reported in a subsequent paper.

EXPERIMENTAL SECTION

Starting materials. The cocoa butter samples were supplied by Cadbury-Schweppes, Ltd. They were prepared from Ghanaian/Nigerian Grade 1 cocoa beans. The roasted cocoa butter was obtained from cocoa beans which were roasted at 145 C for 8 min in a continuous roaster. Cocoa liquor obtained from the roasted beans was hydraulically pressed at 100 C and 7,000 psi to obtain the roasted cocoa butter. The unroasted cocoa butter was obtained from the expeller pressing of whole cocoa beans. The beans were heated with steam to 85 C and held for 20 min before being pressed.

The aromas of the cocoa butter samples were evaluated by two trained flavorists. The roasted sample had a strong, well-rounded cocoa aroma with some burnt characteristics. The unroasted sample had a milder aroma with acidic, fruity, floral and fatty-waxy characteristics. It did not possess the total cocoa aroma.

Flavor isolation. The volatile flavor compounds of both cocoa butter samples were isolated using a semicontinuous, countercurrent, vacuum steam distillation apparatus (4). The volatile flavor compounds were isolated from a total of 80 lb of the roasted cocoa butter and 70 lb of the unroasted cocoa butter.

Water vapor and volatile flavor compounds were condensed in a series of cold traps which were cooled with a dry ice and acetone slurry. The condensate collected in the traps was combined, saturated with sodium chloride and extracted with ethyl ether. The ether extracts were dried over anhydrous Na_2SO_4 and subjected to a preliminary concentration using a 30-plate Oldershaw distillation column. The ether extracts from both cocoa butter samples were concentrated to final volumes of 15 ml using a spinning band distillation apparatus.

The reproducibility of the isolation methodology and its effectiveness in producing flavor isolates representative of the starting material were demonstrated in preliminary studies described by Carlin et al. (5).

Separation of the flavor isolates into acidic, basic and neutral fractions. The flavor isolates were separated into acidic, basic and neutral fractions to facilitate gas chromatographic analysis. Separation into acidic and nonacidic fractions was accomplished by extraction with 10% aqueous Na_2CO_3. The nonacidic fractions were further separated into basic and neutral fractions by extraction with 10% aqueous HCl. All ether solutions of acidic, basic and neutral compounds were dried over anhydrous Na_2SO_4 and concentrated to 5 ml using a spinning band distillation apparatus.

Analysis of the acidic fractions. The aromas of the acidic fractions were evaluated by two trained flavorists. The unroasted acidic fraction had a strong aroma which was characteristic of the C_2-C_5 fatty acids. The aroma of the roasted acidic fraction was much less acidic and lacked the animal character associated with 3-methylbutanoic and pentanoic acids.

A portion of both acidic fractions was quantitatively converted to methyl esters using a BF_3-methanol reagent. The procedure used was essentially the same as that of Metcalfe and Schmitz (6). The esterified acidic fractions were analyzed using a Beckman GC-5 gas chromatograph equipped with a thermal conductivity detector. The injection port and detector temperatures were held at 220 and 250 C, respectively. A 10 ft × 1/8 in. o.d. stainless steel column packed with 10% DEGS on 80/100 mesh Chromosorb W AW DMCS was used for the analysis. The He flow rate was 30 ml/min. The column temperature program was 50 C, held for 5 min, then 2.5 C/min to a final temperature of 180 C.

The comparative gas chromatograms of the esterified cocoa butter fractions are shown in Figure 1. These chromatograms represent quantitative comparisons between the acidic fractions of the roasted and unroasted cocoa butters. The peaks obtained in the gas chromatographic separation of the esterified acidic fractions were accumulatively collected in "hairpin" capillary glass traps according to the method of Thompson (7).

Analysis of the basic fractions. The aromas of the basic fraction also were evaluated by two trained flavorists. Both basic fractions were perceived to contain mainly pyrazines. However, the green-earthy-musty aroma characteristic of some pyrazines was much stronger in the roasted basic fraction. The roasted basic fraction also contained a persistent dark cocoa-honey aroma.

The basic fractions were more complex than the acidic fractions and were subjected to a systematic method of gas chromatographic fractionation in order to obtain pure compounds. The gas chromatograph, injection port and detector temperatures employed in the analysis of the basic fractions were the same as previously described. A 10 ft × 1/8 in. o.d. stainless steel column packed with 10% OV-17 on 60/80 mesh Chromosorb W AW DMCS was used for the first gas chromatographic fractionation of the basic fractions. The He flow rate was 30 ml/min. The column temperature program was 55 C, held for 10 min, then 2.5 C/min to a final temperature of 215 C.

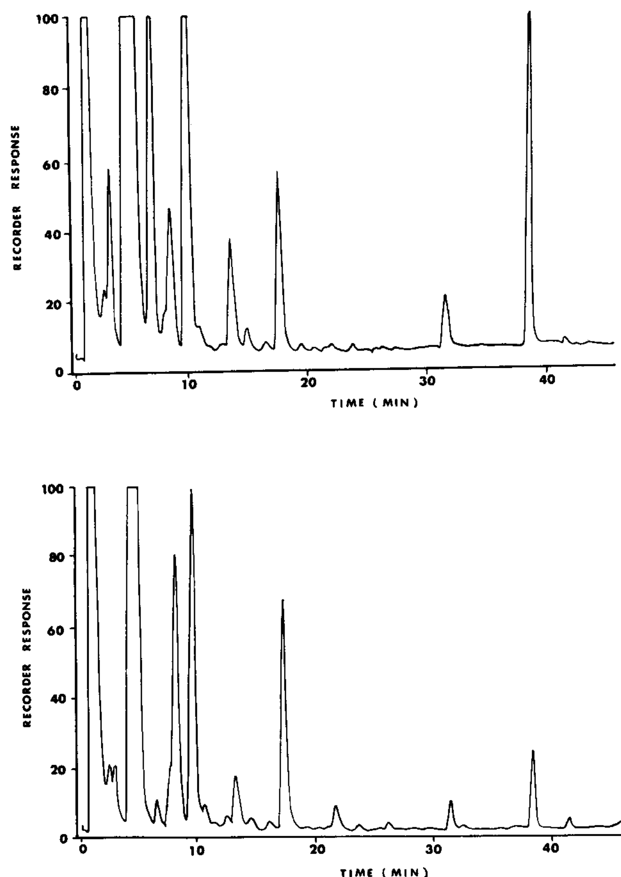

FIG. 1. Comparison of the esterified acidic cocoa butter fractions. Top, unroasted esterified acidic fraction; bottom, roasted esterified acidic fraction.

The comparative gas chromatograms obtained from the first fraction of the basic cocoa butter fractions are shown in Figure 2. The chromatograms represent quantitative comparisons between the basic fractions of the roasted and unroasted cocoa butters. Each chromatogram was divided into fractions which were accumulatively collected as previously described.

Some subfractions obtained from the first fractionation of the basic fractions were subjected to a second fractionation. The second fractionations were conducted using a 10 ft × 1/8 in. o.d. stainless steel column packed with 10% SP-1000 on 60/80 mesh Chromosorb W AW DMCS. The column temperature was programmed to provide maximum resolution for each fraction analyzed. Selected subfractions obtained from the second fractionation, and which seemed impure and existed in sufficient quantities, were subjected to a third fraction-

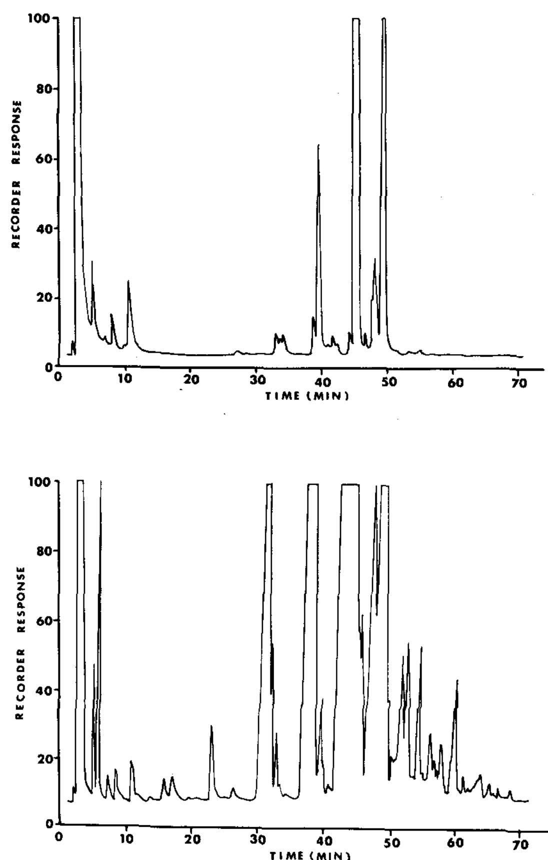

FIG. 2. Comparison of the basic cocoa butter fractions. Top, unroasted basic fraction; bottom, roasted basic fraction.

ation. Third fractionations were conducted using a 10 ft × 1/8 in. o.d. stainless steel column packed with 10% OV-101 on 60/80 mesh Chromosorb W AW DMCS. Again, the column temperature was programmed to provide maximum resolution of the fractions analyzed.

Identification of the volatile flavor compounds. Subfractions obtained from the gas chromatographic fractionation of the acidic and basic fractions were analyzed using a coupled gas chromatograph-mass spectrometer system. The system consisted of a Du Pont Instruments model 21-490 mass spectrometer which was interfaced by a jet separator to a Varian Moduline 2700 gas chromatograph equipped with flame ionization detector. The injection port and detector temperatures of the gas chromatograph were held at 220 and 250 C, respectively. The subfractions were analyzed using either a 10 ft × 1/8 in. o.d. stainless steel column packed with 10% OV-101 on 60/80 mesh Chromosorb W AW DMCS or a 10 ft × 1/8 in. o.d. stainless steel column packed with 10% SP-1000 on 60/80 mesh Chromosorb W AW DMCS. The He flow rate was 30 ml/min. The choice of gas chromatographic column and column temperature program were designed to provide maximum resolution for the fraction analyzed.

Selected subfractions which existed in sufficient quantities also were analyzed using a Beckman Acculab 4 infrared spectrometer. The infrared spectra were obtained in CCl_4 solution using ultra microcavity NaCl cells of 0.1 mm light path.

Compounds were identified by comparing the infrared and mass spectra obtained with those of published spectra. In some cases, organic synthesis was undertaken to confirm the identity of compounds.

Relative concentrations of the compounds identified were approximated based on the integration of gas chromatograms generated from the fractionation of the acidic and basic fractions and the GC-MS analyses. The integrations were conducted using a Hewelett-Packard 5840A GC terminal which was coupled to the detectors of the Beckman GC-5 and Varian Moduline 2700 gas chromatograph.

RESULTS AND DISCUSSION

A total of nine acidic compounds was identified in the roasted and unroasted cocoa butter samples. Two are being reported for the first time in cocoa. Table 1 lists the acids, identified as their methyl esters, in the acidic fractions and the approximate relative concentrations at which they were present. There were significant quantitative differences between the two acidic fractions. The unroasted cocoa butter contained more than three times the concentration of volatile acids than the roasted cocoa butter. The most significant difference was pentanoic acid, which was present in a concentration approximately 18 times higher in the unroasted cocoa butter.

The sensory evaluations of the roasted and unroasted cocoa butter themselves, and of their respective acidic fractions, both indicated that the aroma of the unroasted cocoa butter was more acidic than that of the roasted cocoa butter. The most prominent aroma characteristic of the unroasted cocoa butter was its acidity as determined by trained flavorists. The analysis of the acidic cocoa butter fractions supports the results of the sensory evaluations. The unroasted cocoa butter does contain high concentrations of volatile acids, and this difference was detectable by sensory evaluation. The lower concentration of volatile acids in the roasted cocoa butter is primarily due to the acids being driven off by the higher temperatures which are achieved during the roasting process. The hydraulic pressing of the cocoa liquor at 100 C and 7,000 psi also contributed to the decrease in the concentration of volatile acids. The

TABLE 1

Acidic Compounds Identified in Cocoa Butters from Roasted and Unroasted Cocoa Beans

Compound	Relative Concentrations	
	Roasted	Unroasted
isopentanoic acid	1910	7890
hexanoic acid	330	690
pentanoic acid	20	370
3-methylpentanoic acid[a]	320	170
phenylacetic acid	70	290
octanoic acid	220	200
heptanoic acid	70	130
benzoic acid	20	50
3-hexenoic acid[a]	10	20

[a]Reported for first time in cocoa.

TABLE 2

Basic Compounds Identified in Cocoa Butters from Roasted and Unroasted Cocoa Beans

Compound	Relative Concentrations	
	Roasted	Unroasted
Pyrazines		
tetramethylpyrazine	270	3400
trimethylpyrazine	2620	380
2,5-dimethyl-3-ethylpyrazine	750	40
2,5-dimethylpyrazine	710	60
2-isopropyl-3-methylpyrazine	510	trace
2,6-dimethylpyrazine	490	—
2-acetyl-3-methylpyrazine[a]	390	20
2-ethyl-3,5,6-trimethylpyrazine	310	20
2,6-diethyl-3-methylpyrazine	10	150
6,7-dihydro-5H-cyclopentapyrazine	110	—
methylpyrazine	90	10
2-acetyl-3-ethylpyrazine[a]	90	10
2,5-diethyl-3-methylpyrazine	90	—
2-butyl-3,6-dimethylpyrazine	80	trace
2-methyl-6,7-dihydro-5H-cyclopentapyrazine	80	trace
2-methyl-5-vinylpyrazine	70	—
isopropenylpyrazine	70	—
2-methyl-3-pentylpyrazine	50	trace
2-methyl-6-vinylpyrazine[a]	40	30
2,3-dimethylpyrazine	trace	30
2,3-dimethyl-5-ethylpyrazine	—	30
2,3-dimethyl-5-butylpyrazine[a]	30	—
2,5-dimethyl-3-isobutylpyrazine	30	—
5,6,7,8-tetrahydroquinoxaline[a]	30	—
acetylpyrazine	20	trace
2-isopropyl-5-methylpyrazine[a]	20	trace
2-ethyl-6,7-dihydro-5H-cyclopentapyrazine	20	trace
2,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine	20	—
2,5-dimethyl-3-isopentylpyrazine	20	—
2-pentyl-3,5,6-trimethylpyrazine[a]	20	—
2-(1-propenyl)pyrazine[a]	10	—
2-ethyl-5-methylpyrazine	trace	10
2-ethyl-6-methylpyrazine	—	10
quinoxaline[a]	10	—
2-ethyl-6-propylpyrazine	10	—
2-butyl-3-methylpyrazine[a]	10	10
2-methylquinoxaline[a]	10	—
5,8-dimethyl-5,6,7,8-tetrahydroquinoxaline[a]	10	—
2-ethyl-3-methylpyrazine	trace	—
isopropylpyrazine	trace	—
2-methyl-6-propenylpyrazine[a]	—	trace
5-methyl-6,7-dihydro-5H-cyclopentapyrazine[a]	trace	—
2,3-diethylpyrazine[a]	trace	—
2-(2-furyl)pyrazine	20	—
3,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine	trace	—
Pyrazines (cont.)		
5,7-dimethyl-6,7-dihydro-5H-cyclopentapyrazine[a]	trace	—
5-ethyl-6,7-dihydro-5H-cyclopentapyrazine[a]	—	trace
2,5-dimethyl-3-propylpyrazine	trace	—
2-(2-furyl)-3-methylpyrazine[a]	20	—
5,7-dimethyl-5,6,7,8-tetrahydroquinoxaline[a]	trace	—
2-ethyl-5,6,7,8-tetrahydroquinoxaline[a]	trace	—
2,3,5-trimethyl-6,7-dihydro-5H-cyclopentapyrazine[a]	trace	—
2-methyl-5-pentylpyrazine	trace	—
3,5-dimethyl-2-isobutylpyrazine	trace	—
2-propyl-3,5,6-trimethylpyrazine[a]	trace	—
2-isopropyl-3,5,6-trimethylpyrazine[a]	trace	—
2-butyl-3,5-dimethylpyrazine[a]	—	trace
2-methyl-5-ethyl-6,7-dihydrocyclopentapyrazine[a]	trace	—
2-ethyl-5-methyl-6,7-dihydrocyclopentapyrazine	trace	—
2,3-dimethyl-5-isopentylpyrazine[a]	trace	—
2-butyl-3,5,6-trimethylpyrazine[a]	trace	trace
2-isobutyl-3,5,6-trimethylpyrazine[a]	trace	—
Thiazoles		
2-pentylthiazole[a]	20	—
2-acetyl-5-methylthiazole	10	—
2-isopropyl-4,5-dimethylthiazole[a]	10	—
2-isopropyl-4-methylthiazole[a]	trace	—
Oxazoles		
2-acetyloxazole[a]	10	—
2-isopropyl-4,5-dimethyloxazole[a]	10	—
2-methyl-4,5-dibutyloxszole[a]	10	—
4,5-dimethyloxazole	trace	—
2-methyl-4-ethyl-5-propyloxazole[a]	trace	—
2,5-dimethyl-4-butyloxazole[a]	trace	—
2-methyl-4-ethyl-5-butyloxazole[a]	trace	—
2-butyl-4-methyl-5-ethyloxazole[a]	trace	—
4,5-dibutyloxazole[a]	trace	—
Pyridines		
2-hydroxypyridine[a]	1060	—
2-acetylpyridine	30	trace
3-butylpyridine[a]	10	—
3-phenylpyridine	10	—

[a]Reported for the first time in cocoa.

steam treatment, which the beans used to produce the unroasted cocoa butter were subjected to, represented a significantly milder heat treatment and did not result in as great a decrease in the concentration of volatile acids.

A reduction in the concentration of volatile acids during the roasting of cocoa beans has been reported previously by Rohan and Stewart (8) and Bonar, Rohan and Stewart (9). Lopez and Quesnel (10) have stated that chocolate samples prepared from cocoa beans containing high concentrations of the C_3-C_5 fatty acids had inferior flavors. The reduction in the concentration of volatile acids which occurs during the roasting process is considered to be an important step for the development of good cocoa flavor in the roasted cocoa bean.

A total of 83 basic compounds was identified in the roasted and unroasted cocoa butter samples. The compounds identified included 62 pyrazines, 9 oxazoles, 4 thiazoles, 4 pyridines and 4 miscellaneous compounds. Forty-five of the basic compounds are being reported for the first time in cocoa. Table 2 lists the basic compounds identified and the approximate relative concentrations at which they were present. All of the compounds listed were identified in the basic cocoa butter fractions.

Pyrazines were present in greater numbers and at higher concentrations in the roasted cocoa butter. Of the 62 pyrazines identified, 57 were identified in the roasted cocoa butter and only 27 in the unroasted sample. The roasted cocoa butter contained approximately a two times higher concentration of pyrazines than the unroasted cocoa butter. Pyrazines are an extremely important class of food flavor compounds. Their occurrence in foods and pathways of formation has been reviewed by Maga and Sizer (11,12). Pyrazines are significant contributors to the flavor of heat treated foods. However, they also have been isolated from food systems that have not undergone heat treatment, indicating that biological pathways of formation do exist. Reineccius et al. (13) and Keeney (14) demonstrated that the concentration of pyrazines generated during the roasting of cocoa beans increased as a function of increasing temperature and duration of roast. The formation of pyrazines was clearly favored in the production of the roasted cocoa butter. Keeney (14) stated that differences in flavor among chocolates can be attributed in part to the presence or absence of large amounts of alkylpyrazines and in qualitative differences between their alkylpyrazine fractions. The quantitative and qualitative differences between the pyrazines identified in the cocoa butter samples are probably the most important factors contributing to their aroma differences and to the cocoa aroma of the roasted cocoa butter.

The most abundant pyrazine identified was tetramethylpyrazine, which existed at an extremely high concentration in the unroasted cocoa butter and only a moderate level in the roasted cocoa butter. Tetramethylpyrazine accounted for over 90% of the pyrazine content of the unroasted cocoa butter. This is in agreement with Reineccius et al. (13), who found that tetramethylpyrazine accounted for almost all of the pyrazine content of cocoa beans roasted for 30 min at 70 C. Tetramethylpyrazine has been identified in fermented, unroasted cocoa beans (13,15). Besides thermal generation, tetramethylpyrazine could be formed in cocoa beans through biosynthetic reactions. Kosuge and Kamiya (16) identified tetramethylpyrazine as a metabolic product of a strain of *Bacillus subtilis*. Several species of this organism were identified in a fermenting mass of cocoa beans by Ostovar (17).

The oxazoles and thiazoles identified were present in only the roasted cocoa butter. The presence of several of these compounds was confirmed through synthesis (18). Oxazoles and thiazoles possess interesting sensory characteristics and are high impact flavor compounds. Oxazoles could possibly be formed through the Strecker degradation of aminoketones which result from the condensation of α-dicarbonyl compounds with amino acids (19). They might also form through reactions between amino acids (20). Maga (21) has reviewed the occurrence of thiazoles in foods and possible pathways of formation. Thiazoles have been identified in several heat treated foods and could possibly form through the interaction of sulfur-containing amino acids and carbonyl-containing compounds. Thiazole derivatives have been identified as volatile components of thermally degraded thiamine (22). Biosynthetic pathways of thiazole formation could also exist (23). 2-Pentylthiazole was found to have a strong fatty, green and sweet aroma, which could contribute to cocoa butter flavor (18).

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Heterogeneous Catalytic Hydrogenation of Canola Oil Using Palladium

N. Hsu, L.L. Diosady*, W.F. Graydon and **L.J. Rubin**
Department of Chemical Engineering, University of Toronto, Toronto, Ontario, Canada M5S 1A4

The hydrogenation of canola oil was studied using palladium black as a potential catalyst for producing partially hydrogenated fats with low *trans*-isomer content. Pressure (150-750 psig) appeared to have the largest effect on *trans*-isomer formation. At 750 psig, 90 C and 560 ppm metal concentration, a maximum of 18.7% *trans* isomers was obtained at IV 53. A nickel catalyst produces about 50% *trans* isomers at the same IV. For palladium black, the linolenate and linoleate selectivities were 1.2 and 2.7, respectively. The maximum level of *trans* isomers observed ranged from 18.7% to 42.8% (150 psig). Temperature (30-90 C) and catalyst concentration (80-560 ppm) affected the reaction rate with little effect on *trans*-isomer formation and selectivities. At 250 psig and 50 C, supported palladium (5% Pd/C) appeared to be twice as active as palladium black. At 560 ppm Pd, 5% Pd/C produced 30.2% *trans* (IV 67.5), versus 19.0% *trans* for palladium black (IV 68.9). Respective linoleate selectivities were 15 and 6.6, while linolenate selectivities were approximately unity. Analysis of the oil samples by neutron activation showed approximately a 1 ppm, Pd residue after filtration.

The search is still on for an active, heterogeneous catalyst for hydrogenation of edible oils with production of a low level of *trans* isomers. The need for such a catalyst arose following a Canadian study which reviewed the health effects of these isomers (1). This subject was reviewed thoroughly by Applewhite (2). In his review it was shown that the studies of the health effects of *trans* isomers were inconclusive. The FDA recently commissioned the Federation of American Societies for Experimental Biology to undertake a study of *trans* fatty acids (3) in the hope of settling this controversial issue. Thus, we feel it would be prudent to develop alternative catalysts which would minimize the formation of *trans* fatty acids. Such a development would, in any case, offer the processor an alternative, should one be needed, for this or any other reason.

In an earlier review of catalysts (4), it was reported that heterogeneous palladium catalysts were unsuitable for the hydrogenation of triglycerides because they were nonselective and produced large quantities of *trans* acids. More recent work indicates that, in general, palladium forms more *trans* isomers than nickel (5), especially under conditions normally employed with the latter (6). Thus, we initially investigated the homogeneous catalytic hydrogenation of canola oil using a palladium complex. It had been reported by Itatani and Bailar (7) that the mixture of dichlorobistriphenylphosphine palladium (II) and stannous (II) chloride dihydrate was a very active homogeneous catalyst for the hydrogenation of soybean oil methyl esters. Furthermore, at 575 psi and 60 C, a total *trans* content of less than 20% was observed. We used this catalyst mixture to hydrogenate canola oil at 500 psig and 110 C. After 5 hr of reaction time the IV dropped 12 units. A black precipitate, most likely palladium, was present in the partially hydrogenated oil. Itatani and Bailar (7) reported that some of their runs produced a precipitate. In another report (8), the same authors observed a black precipitate following the hydrogenation of soybean oil methyl ester using the platinum analog of the palladium complex. The precipitate, assumed to be platinum black, was then used in a run, but it proved to be relatively inactive. We observed that our precipitate, when used alone in the hydrogenation of canola oil, was very active at 750 psig and 70 C. The homogeneous palladium catalyst subsequently was abandoned, and palladium black was made the catalyst of choice. The objective of our study was, therefore, to evaluate the performance of palladium with respect to pressure, temperature, concentration and catalyst support during the hydrogenation of canola oil.

The earliest published work on the hydrogenation of any edible oil in which palladium was used was in 1953; in it, the promoter effect of platinum and palladium on nickel was examined (9). It was found that the addition of platinum increased the bonding strength of hydrogen to the catalyst surface, whereas addition of palladium decreased the bonding strength. Zajcew (10) hydrogenated castor oil to castor wax using 5% and 1% palladium on carbon. Although palladium on carbon was used by Zajcew in subsequent reports (11,12), it was for the hydrogenation of soybean and cottonseed oil. In almost all cases, hydrogenation was accompanied by 20-50% *trans*-isomer formation. The lowest *trans* content reported was 15.0% at IV 67.1 (11). The catalyst used was palladium (200 ppm) in the form of 1%

*To whom correspondence should be addressed.