implication is that modular storage does not increase toxin levels of spindle first-picked cotton.

In contrast, a significant increase in aflatoxins was observed in all modules containing ground-gleaned seed cotton (Table II). The overall increases on a module by module comparison ranged from 12-232% with an average increase of approximately 67%. There also was a trend toward greater increases in total aflatoxins in seed stored in the center of module. The increase here was approximately 134% compared to 50% for seed stored on top of the module and 34% for that stored in the bottom strata.

It is well established that cottonseed recovered by ground-gleaners is of poor quality, and such seed harvested in chronic aflatoxin areas in Arizona will almost always contain aflatoxins (6). This seed apparently falls into the category that has been described as being of low quality and subject to deterioration regardless of moisture level (2). Since no temperature increase was noted in any of these modules, we must assume that moisture remained below 12%. Since temperature measurements were discontinued after the first week, changes in temperature and moisture after several weeks of modular storage were not determined. It is possible that in selected areas of the modules a moisture transfer could have occurred between wet fiber or green trash and seed. Such a moisture increase would enhance microbial activity and promote toxin formation.

Our results show that modular storage of ground-gleaned cotton is ill advised.

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Homogeneous Catalytic Hydrogenation of Soybean Oil: Palladium Acetylacetonate

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ABSTRACT

Soybean oil was hydrogenated with palladium acetylacetonate at 60-170 C, 150 psi hydrogen and 1-60 ppm palladium. The best linolenate selectivity (K_{Le}/K_{Lo} = 3.5-3.7) was found at 80-120 C. At 120 C palladium acetylacetonate hydrogenated faster than the heterogeneous Pd-on-carbon catalyst. *Trans* isomerization with the homogeneous catalyst was much higher compared to Pd-on-carbon catalyst. The low activity of the palladium complex at low temperatures was improved with the addition of triethylaluminum. Among other metal acetylacetonates tested only nickel and chromium were mildly active, whereas cobalt and copper were devoid of catalyst activity.

INTRODUCTION

One of the program objectives at this laboratory is to improve the stability of soybean oil through selective hydrogenation. Copper catalysts previously have been shown to be more selective than the commonly employed nickel catalysts (1). Homogeneous nickel acetylacetonate catalyst is more selective than heterogeneous nickel catalyst (2), but this homogeneous catalyst is active only in the presence of methanol solvent, and triglycerides are simultaneously transesterified to methyl esters.

Now we have observed that palladium acetylacetonate catalyzes selective hydrogenation of soybean oil. Since we started our study, another group reported on this catalyst (3). We also have studied acetylacetonates of several group VIII metals. Acetylacetonate complexes of Cu (III), Co (II) and Co (III) were devoid of catalytic activity, whereas Ni (II) and Cr (III) acetylacetonates showed only slight activity for the hydrogenation of soybean oil.

EXPERIMENTAL

Materials

Central Soya Co., Inc. (Fort Wayne, Indiana) supplied the refined and bleached soybean oil (IV 136.8). Acetylacetonate complexes of Pd (II), Ni (II) (Strem Chemicals Inc., Newburyport, Massachusetts); Co (II), Co (III), Cr (II) (Pfaltz & Bauer, Inc., Stamford, Connecticut); and Cu (II) (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin) were purchased from commercial sources.

Hydrogenation

Palladium acetylacetonate dissolved in 75 g soybean oil was placed in a 150-ml magnetically stirred Magna-Dash autoclave which was electrically heated under nitrogen pressure. When the reaction temperature was reached, the stirrer was stopped and nitrogen was vented to the atmosphere. Hydrogen (150 psi) gas was admitted into the reactor from an external reservoir (250 ml) through a pressure regulator valve, which maintained a constant pressure (150 psi hydrogen + 15 psi nitrogen) in the autoclave. The reaction started when stirring began, as no hydrogen uptake was observed without stirring. The extent of hydrogenation was followed by measuring the drop in hydrogen pressure in the external reservoir and by taking samples at intervals for analysis.

Analytical Methods

The hydrogenated soybean oil containing the catalyst was converted directly to methyl esters with sodium methoxide catalyst, according to the method of Christopherson and

TABLE I

Hydrogenation of Soybean Oil with Palladium Acetylacetonate Catalyst[a]

Expt. No.	Pd (ppm)	Temp. (C)	Time (min)	Fatty acid composition, %[b]					Catalyst activity (ΔIV/min/ppm Pd) × 10^2	*Trans* % (%t/ΔIV)	Selectivity	
				St	M	D	T	IV			K_{Le}/K_{Lo}	K_{Lo}/K_{Ol}
				3.5	22.0	55.0	8.6	136.8	—	—	—	—
1	60	60	164	4.7	30.1	48.3	5.9	125.0	0.1	4.2 (0.36)	2.1	3.5
			235	5.9	42.6	37.8	2.6	108.9	0.2	9.8 (0.35)	2.4	6.2
2	60[c]	60	23	4.3	31.3	48.0	5.4	124.2	0.9	13.9 (1.10)	2.3	5.4
			44	4.8	38.5	42.5	3.2	115.1	0.8	19.7 (0.91)	2.7	7.7
			70	5.6	45.3	36.2	1.8	106.4	0.7	30.6 (1.01)	2.8	8.2
			114	6.8	53.5	27.9	0.7	96.2	0.6	40.1 (0.99)	2.9	9.6
3	15	80	25	4.0	39.2	43.4	2.4	115.2	5.8	24.8 (1.15)	3.5	16.4
			43	4.1	47.4	36.2	1.2	106.6	4.7	32.8 (1.09)	3.4	23.2
			66	4.1	53.3	31.3	0.4	101.1	3.6	39.8 (1.11)	4.2	42.9
			100	4.3	58.2	26.3	0.3	96.4	2.7	46.2 (1.14)	3.7	44.2
4	9	120	12	3.7	36.7	45.8	2.9	118.5	16.9	30.4 (1.66)	3.7	31.1
			20	3.9	46.1	37.6	1.3	108.2	15.9	44.5 (1.56)	3.6	27.1
			30	4.1	56.1	28.3	0.4	98.3	14.3	54.6 (1.42)	3.6	39.2
			45	4.7	63.3	21.0	0.0	90.3	11.5	59.7 (1.30)	—	—
5	10[d]	120	25	6.5	35.7	42.7	4.3	115.9	8.4	14.4 (0.69)	2.0	3.4
			38	8.1	41.0	36.5	3.0	106.3	8.0	26.4 (0.87)	2.0	3.3
			53	10.2	46.7	30.3	1.9	97.6	7.4	29.0 (0.74)	2.0	4.0
			70	12.1	50.7	25.0	1.3	90.3	6.6	33.0 (0.71)	2.0	4.4
6	30[e]	120	56	3.6	38.4	44.4	2.7	117.0	1.2	35.5 (1.79)	3.5	56.3
			105	3.8	48.3	36.0	1.0	106.5	1.0	53.0 (1.75)	3.7	54.9
			150	4.0	52.5	32.0	0.6	102.2	0.8	58.6 (1.72)	3.7	47.4
7	2.5	150	21	4.7	44.3	38.1	1.9	109.1	52.8	35.3 (1.27)	3.0	12.5
			30	6.0	54.6	28.1	0.7	97.5	52.4	46.0 (1.17)	3.0	15.1
			40	6.8	61.5	20.8	0.0	89.0	47.8	57.1 (1.19)	—	—
			60	9.1	65.6	14.4	0.0	81.4	36.9	64.5 (1.16)	—	—
8	1	170	11	3.9	29.3	49.8	5.9	126.9	90.0	12.2 (1.23)	2.5	5.7
			24	4.4	35.3	45.1	4.3	119.7	71.3	22.2 (1.30)	2.4	8.4
			65	5.5	42.8	38.5	2.4	109.8	41.5	31.0 (1.15)	2.6	8.2
			100	5.9	45.8	35.6	2.0	106.3	30.5	34.8 (1.14)	2.5	8.9

[a] H_2 at 150 psi.

[b] Abbreviations: St = Stearate; M = Monoene; D = Diene; T = Triene; IV = Iodine value; Le = Linolenate; Lo = Linoleate, and Ol = Oleate.

[c] 1.0 ml of 25% triethyl aluminum in heptane added.

[d] Catalyst 5% Pd-on-carbon.

[e] H_2 at 30 psi.

Glass (4). This method was modified by replacing hexane with diethylether. Fatty acid compositions were determined by gas liquid chromatography (GLC) with packed columns (EGSS-X), and the iodine values (IV) were calculated. The percentage of isolated *trans* was measured by comparing the infrared absorption of methyl esters at 966 cm^{-1} with a methyl elaidate standard. Linolenate to linoleate selectivity (K_{Le}/K_{Lo}) and linoleate to oleate selectivity (K_{Lo}/K_{Ol}) ratios were determined by a digital computer assuming consecutive reactions; i.e., triene → diene → monoene → stearate (5).

RESULTS

Soybean oil was hydrogenated with palladium acetylacetonate catalyst, and three of the four operating variables (catalyst concentration, temperature and pressure) were changed to study their effect on selectivity, activity and *trans*-isomer formation. The results are shown in Table I.

Catalyst Activity

Palladium acetylacetonate effectively catalyzed the hydrogenation of soybean oil with as little as 1 ppm metal (Expt. 8). The activity of the catalyst expressed as drop in IV/min/ppm Pd increased with temperature and pressure. The homogeneous catalyst showed only slight activity at 60 C, but its activity improved with the addition of triethyl aluminum (Expts. 1 and 2). Apparently, the organoaluminum-palladium complex is a better catalyst than palladium acetylacetonate by itself. Under similar conditions of hydrogenation, the soluble catalyst was more active than the insoluble Pd-on-carbon catalyst (Expts. 4 and 5).

Selectivity

Optimum linolenate selectivity (K_{Le}/K_{Lo} = 3.4-4.2) was obtained at 80-120 C. This high selectivity compares favorably with the heterogeneous catalyst that gave a selectivity of 2.0 under similar conditions. Linoleate selectivity was poor at low temperature (Expt. 1) but improved with temperature. Linoleate selectivity also improved when pressure was reduced to 30 psi (Expt. 6). Both linolenate and linoleate selectivities decreased above 120 C. For example, increasing the temperature from 120 to 150 C caused the linolenate selectivity to drop from an average value of 3.6 to 3.0. Further increase in temperature to 170 C lowered the selectivity to 2.5, a value which is only slightly better than the 2.0 normally obtained with commercial nickel catalysts (6, 7). The low linolenate selectivity of palladium acetylacetonate at 60 C was improved with the addition of triethyl aluminum.

Isomerization

To minimize winterization losses and to increase liquid oil yields, it is desirable to keep *trans* isomerization to a minimum. Heterogeneous palladium catalysts generally produce higher *trans*-isomer levels than nickel catalysts. The homogeneous catalyst of this study produced even higher amouns of *trans*-isomers. As expected, isomerization measured as percentage *trans*-isomers formed for unit IV drop increased with temperature, and lowering the pressure had a similar effect. Addition of triethyl aluminum to the soluble catalyst increased isomerization.

Acetyl Acetonates of Other Metals

Other metal acetylacetonates were tried for selective hydrogenation of soybean oil (Table II). Copper and cobalt complexes showed no activity. Chromium showed slight activity, but the reaction was completely nonselective. Nickel acetylacetonate had a linolenate selectivity of 2.3, but the activity is only moderate compared to heterogeneous nickel catalysts. Unlike the palladium complex, which was soluble in soybean oil, Ni, Cr, Co and Cu acetyl acetonates were only partially soluble. It is therefore not clear whether the soluble or insoluble complex contributed to catalyst activity. However, hydrogenation occurred at approximately half the rate when nickel concentration was halved. If the soluble complex were the sole active catalyst, the reaction should have occurred at the same rate.

DISCUSSION

One approach to improving flavor stability of soybean oil is to reduce the linolenate content by selective hydrogenation, and we have been engaged in a long-term study to find new catalysts that have potential for better selectivity and activity. Palladium acetylacetonate was found to meet these requirements. Commercially employed nickel catalysts have a linolenate selectivity of about 2 (6, 7). Heterogeneous palladium catalysts are more active than nickel, but have similar linolenate selectivity (8-11). Palladium catalyst of this study (Table I, Expt. 4) exhibited a significantly higher linolenate selectivity of 3.7. As a result of this higher selectivity, soybean oil hydrogenated to an IV of 110 would contain about 1% linolenic acid as opposed to 3%

TABLE II

Hydrogenation of Soybean Oil with Metal Acetylacetonate Catalysts[a]

Catalyst	Metal concn. (%)	Temp. (C)	Time (min.)	Fatty acid composition, %[b]					% *Trans*	Selectivity	
				St	M	D	T	IV	(%t/ΔIV)	K_{Le}/K_{Lo}	K_{Lo}/K_{Ol}
$Ni(acac)_2$	0.1	180	55	5.3	42.2	38.3	3.0	110.5	13.0 (0.49)	2.2	7.3
			80	6.3	46.1	34.7	2.1	105.2	15.1 (0.48)	2.3	7.6
			110	7.3	49.8	30.3	1.5	99.1	17.5 (0.46)	2.3	6.9
$Cr(acac)_3$	0.25	180	50	5.6	26.5	49.2	7.6	127.9	–	0.9	1.4
			120	8.0	30.5	44.1	6.3	119.1	7.0 (0.40)	1.1	1.5
$Co(acac)_2$	0.05	170						no reaction			
$Co(acac)_3$	0.05	200						no reaction			
$Co(acac)_2$	0.1	175						no reaction			

[a] H_2 at 150 psi.

[b] Abbreviations: St = Stearate; M = Monoene; D = Diene; T = Triene; IV = Iodine value; Le = Linolenate; Lo = Linoleate; Ol = Oleate, and acac = Acetylacetonate.

found in nickel-catalyzed, hydrogenated oil. Only 9 ppm of palladium metal was required for effective hydrogenation. Commercially, nickel catalysts are employed in the range of 200-500 ppm. Much higher *trans*-isomer contents were found in soybean oil hydrogenated with homogeneous palladium catalyst than those normally found with nickel catalysts. Although the higher activity and greater selectivity might provide improved stability of the hydrogenated oil, the increased *trans* content will reduce the yield of liquid oil. The catalyst in this study formed higher *trans*-isomers than heterogeneous palladium-on-carbon catalyst (Table I, Expts. 4 and 5). This unusual property might be useful in production of products such as shortenings and margarines, where the high *trans* content imparts desirable plasticity.

As little as 1 ppm palladium effectively catalyzed hydrogenation of soybean oil at 170 C; at this high temperature the catalyst appeared to decompose. Some black insoluble material was collected when the hydrogenated sample was filtered. At 150 C, some decomposition was visible, but at 120 C and below there was no decomposition of the catalyst. Soybean oil and hydrogenated soybean oil containing palladium acetylacetonate (Table I, Expt. 4) were submitted to a commercial testing laboratory for analysis after filtration. The initial oil contained 6 ppm Pd and the hydrogenated oil showed 5 ppm Pd. These values indicate that the catalyst was not decomposed during hydrogenation. Nickel acetylacetonate also decomposes at high temperatures, and the decomposed precipitate is catalytically inactive (2).

Heterogeneous catalysts have the advantage of ease of separation. With homogeneous catalysts such as palladium acetylacetonate, an extra step, e.g., an acid wash, is necessary for its removal. Alternatively, homogeneous catalysts could be heterogenized (12) by bonding them to carriers such as silica. Whether such a heterogenized catalyst would still be as active and selective as the homogeneous catalyst remains to be determined. The high linolenate selectivity and activity of palladium acetylacetonate demonstrated in this study warrants further investigation for possible commercial application.

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Variations in Fat Content and Lipid Class Composition in Ten Different Mango Varieties

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ABSTRACT

The kernels of 10 different mango varieties were extracted. The physico-chemical characteristics and lipid class composition of fats were studied. The fat content of mango kernels grown under the soil and climatic conditions of Bangladesh varied from 7.1% to 10%, depending on the variety. The total lipid extracts were fractionated into lipid classes by a combination of column and thin layer chromatography (TLC). The hydrocarbon and sterol esters varied from 0.3% to 0.7%, triglycerides from 55.6% to 91.5%, partial glycerides from 2.3% to 4% and free sterol from 0.3% to 0.6%. Free fatty acids amounted to 3.0-37% as oleic; glycolipids were 0.6-1.2% and phospholipids 0.11-0.8%. The fatty acid composition of triglyceride (TG) fractions was analyzed by gas liquid chromatography (GLC). Palmitic acid varied from 7.9 molar % to 10.0 molar %, stearic from 38.2% to 40.2%, oleic from 41.1% to 43.8%, linoleic from 6.0% to 7.6%, linolenic from 0.6% to 1.0% and arachidic acid from 1.7% to 2.6%. TLC revealed the presence of lyso-phosphatidylcholine, phosphatidylcholine, phosphatidylinositol, phosphatidylethanolamine and phosphatidic acid in the phospholipid fraction.

INTRODUCTION

Bangladesh occupies an important position among the mango growing countries in the world. A wide variety of mango (*Mangifera indica* L.) are extensively cultivated in Bangladesh with an annual production of ca. 500 thousand tons (1). It is considered the king of all indigenous fruits of the tropics. The ripe stone fruit is widely used for eating directly and for the manufacture of jam and jelly. The mango seeds are a waste product and are thrown away after being separated from the pulp. The seed represents up to 24% of the weight of the fruits and contains 7.1-10% fat depending on the variety.

The characteristics of mango kernel fat as reported by several workers (2-6) show that the fat is edible and has some resemblance to cocoa butter. Little attention (7) has been given to individual lipid components in mango kernel fat, although some researchers have suggested that they play a significant role in the stability and quality of vegetable fats (8-11).

Because the average fat content of mango seed is ca. 10%, the total annual production of mango fat in Bangladesh is ca. 10,000 tons. Thus, if properly collected and used, mango fat could be an abundant potential source of vegetable fat. The composition of fat varies with the source (12) and depends on factors such as climatic conditions, soil type, maturity of plant and variety (13,14).

The objective of this study is to evaluate the variations in fat content and lipid class composition in different mango varieties grown in Bangladesh.

MATERIALS AND METHODS

Ten varieties of ripe mango (Brindaboni, Fazli, Kalabau, Kanchamitha, Kuipahari, Lakhanvoge, Lengra, Mohanvoge, Misrakanta and Ranipasand) were collected from mango growers in Rajshahi.