Trisaturates in the Hydrogenation of Canola Oil with a Commercial Nickel Catalyst

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ABSTRACT

Refined and bleached Canola oil was hydrogenated with Pricat 9906 catalyst to an iodine value of 65 using various temperatures, pressures and catalyst concentrations. Hydrogenation with this catalyst resulted in great differences in SFI curves of fats with the same IV. Hydrogenation rate, dropping point, trisaturate content and linoleate selectivity were determined. All of the oils hydrogenated to IV 65 contained almost the same amount of solid fat at 20 C. For this reason, the crystal structure of the fats was examined by X-ray diffraction at 20 C. The catalyst was found to be non-selective. Increased selectivity can be obtained by careful temperature and pressure control. Reactivity also is temperature and pressure dependent. High trisaturate content increased instability by promoting formation of β crystals. The catalyst had excellent filterability characteristics.

INTRODUCTION

Catalysts used in hydrogenation are judged by their activity, selectivity, resistance to catalyst poisons and filtration characteristics. Good activity and filterability are of economic importance. Resistance to catalyst poisons is advantageous in the hydrogenation of rapeseed oils (1). Selectivity is of importance in the stability of the end product and for the formation of solid fat. Catalyst surface area, Ni/NiO ratio and pore size determine activity and selectivity. In catalysts with narrow pore size, high concentrations of saturated species may inhibit further hydrogenation at that site (2, 3, 4, 5).

Selectivity also can be achieved by employing selective hydrogenation conditions.

Non-selective hydrogenation conditions and non-selective catalysts may form trisaturates. Trisaturates and especially tristearate have high melting points. Tristearate is sparingly soluble in unsaturated oils, and even a relatively low content of tristearate will increase the melting point (2). Trisaturates crystallize in the β form and are undesirable in the manufacture of margarine.

Trisaturate content traditionally has been determined by the addition of mercuric acetate to the double bonds in other triglycerides and then separation of trisaturates by column chromatography using Florisil (6). A more recent method has employed ozonolyses with capillary gas chromatography (7). In the present study, separation of the trisaturates was achieved by silver nitrate-coated Chromarods-S with quantification by the flame ionization detector of an Iatroscan TH-10 analyzer.

This study deals with the effect of varying process conditions on activity, selectivity of the reaction and composition of hydrogenated Canola oil using the commercial nickel catalyst Pricat 9906.

EXPERIMENTAL

Refined and bleached Canola oil was hydrogenated with Unichema catalyst 9906 to an iodine value of approximately 65 using various temperatures, pressures and catalyst concentrations. A 2 L Parr pressure reaction apparatus was used with a charge of 1 kg of oil and agitation speed of 610 rpm.

Solid fat content was determined by NMR (8). Melting points were determined by the Mettler FP3 automatic dropping point apparatus (9).

The total *trans* content was determined according to AOCS method Cd 14-61.

Melting curves were obtained using a DuPont thermal analyzer series 99 with a heating rate of 5 C/min.

Linoleate selectivity was calculated using the computer program of AOCS recommended practice Tz 16-79.

Crystal structure was determined by X-ray diffraction analysis using a Diffractis 601 X-ray generator and Guinier camera model FR 552 of Enraf-Nonius, Delft, The Netherlands.

Each of the partially hydrogenated Canola oil samples was transesterified with BF_3-MeOH (10), and the resulting methyl esters were analyzed by gas liquid chromatography (GLC). The analytical GLC was executed on stainless steel, wall-coated, open-tubular columns, 47 m × 0.25 mm ID coated with SILAR-5CP, operated in a Perkin-Elmer 910 series apparatus with FID. The peaks were recorded on a Fisher Ricordal series 5000 recorder with a stepping-pen integrator for area determination.

Trisaturated glycerides were determined by silver nitrate TLC on Chromarods-S. Clean Chromarods-S were immersed in a 2.5% solution of silver nitrate in acetonitrile for 15 min, then activated by heating in an oven at 120 C for 3 hrs. The rods were allowed to cool to room temperature in a desiccator covered with aluminum foil. These rods were spotted with a sample, developed for 30 min in benzene, then dried in the oven (120 C) for 3 min. The rods were scanned by FID in an Iatroscan TH-10 apparatus (11). Peak areas were determined by using an integrator/calculator (Model AAG, Technicon Instruments, Chauncey, New York). After use, the rods were cleaned for re-use by soaking in concentrated nitric acid overnight, rinsing with water and then acetone, and passage through the flame in the Iatroscan.

A standard curve of Iatroscan chromatogram peak areas vs amount of GS_3 spotted on Chromarod was obtained by developing and scanning various concentrations of authentic tristearin. The results are depicted in Figure 1. Each of the various concentrations were analyzed on 10 different

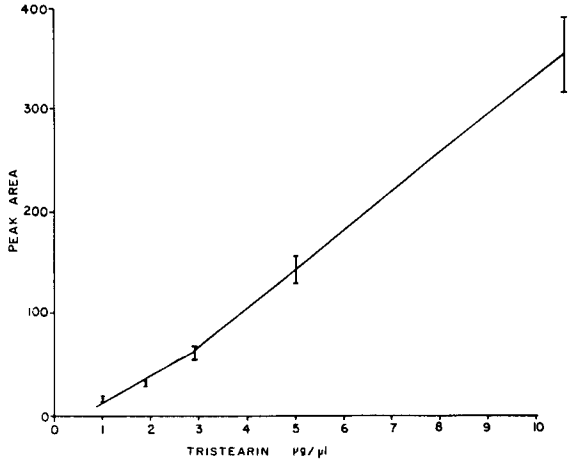

FIG. 1. A plot of $AgNO_3$-Iatroscan peak area versus the amount (μg) of authentic tristearin spotted on the $AgNO_3$-Chromarods. The $AgNO_3$-Chromarods were developed in benzene.

rods, and the range of peak areas obtained is indicated by the bar lines in Figure 1.

For the determination of GS_3 content, working solutions of the partially hydrogenated Canola oil samples were prepared by dissolving accurately weighed oil samples in $CHCl_3$. The concentrations of these samples were about 17.0 to 18.0 μg oil/μl of $CHCl_3$. Exactly 1 μl of these samples were spotted on the $AgNO_3$-Chromarods, developed and the GS_3 peak areas obtained as described earlier. Each sample was analyzed on 10 different rods, and the average of the 10 peak areas was determined. The amounts of GS_3 were determined using the standard curve. Hence, the percentage of GS_3 was calculated from the amount of oil sample spotted on the rod. The $AgNO_3$-Iatroscan chromatograms of the five samples are given in Figure 2. The position of the GS_3 in Canola oil samples was identified by spiking the samples with authentic tristearin.

RESULTS AND DISCUSSION

Activity. Table I shows the activity of catalyst Pricat 9906. Hydrogenation was attempted at 150 C and 276 kPa with 0.2% catalyst but activity was extremely low and, therefore, this was not pursued further. Higher temperatures markedly increased the activity especially when the pressure was also high. At 200 C and 48 kPa activity decreased. Mass transfer of hydrogen appears to be the limiting factor as indicated by the fact that a 0.1% catalyst concentration hardly decreased the activity. Lowering the catalyst concentration to 0.1% at 175 C and 138 kPa slowed down the activity drastically and again this was not pursued further.

Selectivity. Table I shows the linoleate selectivities computer calculated from the results of the fatty acid analyses by GLC. Selectivity ranged from 4.4 to 13.8 and *trans* content from 22.3 to 42.6. The correlation coefficient between selectivity and *trans* content was .9928. Selective hydrogenation (200 C and 48 kPa) produced almost twice as much *trans* fatty acids for fats of the same iodine value as did non-selective hydrogenation (160 C and 276 kPa).

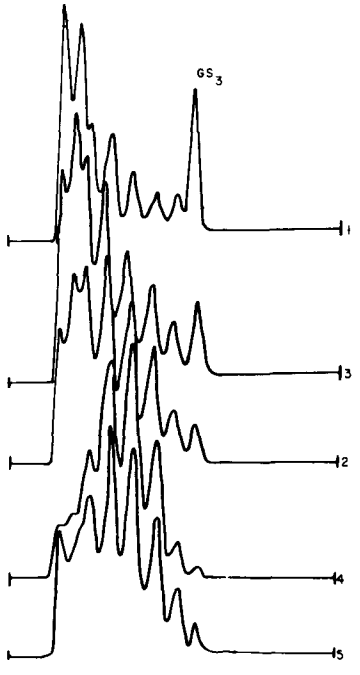

FIG. 2. $AgNO_3$-Iatroscan chromatograms of five partially hydrogenated Canola oil samples. Curve 1: 160 C, 276 kPa; Curve 2, 175 C, 138 kPa; Curve 3: 175 C, 276 kPa; Curve 4: 200 C, 48 kPa; Curve 5: 200 C, 48 kPa. Experimental conditions as listed in text.

TABLE I

Activity and Characteristics of Canola Oil Hydrogenated with Catalyst Pricat 9906

Sample no.	Hydrogenation conditions: Temp. (C)	Pressure: kPa	Pressure: psi	Catalyst concentration (%)	Iodine value	Hydrogenation time (min)	Activity (Δ IV/min)	Linoleate selectivity	Total isolated trans (%)	Trisaturates (%)	Dropping point (C)	Polymorphic forms
1	160	276	40	0.2	65.8	60	0.87	4.4	22.3	14.5	59.1	β
2	175	138	20	0.2	66.5	42	1.23	10.7	35.0	4.8	50.0	β
3	175	276	40	0.2	64.9	30	1.77	7.7	30.9	10.7	54.6	β
4	200	48	7	0.2	64.2	70	0.77	13.8	42.6	3.4	42.8	β′–β
5	200	48	7	0.1	65.1	72	0.73	11.6	38.9	4.1	48.3	β–β′

Trans fatty acids = 2.1267 linoleate selectivity + 13.439, r=.9928.
Trisaturate content = −1.299 linoleate selectivity + 20.02, r=−.9750.
Dropping point = 1.198 trisaturate content + 41.97, r=.9404.

Trisaturate content. Trisaturate analyses were first attempted by means of addition of mercuric acetate to the residual double bonds in other triglycerides, followed by column chromatographic separation. Unfortunately, the trisaturate fractions were all contaminated by fatty acids containing one double bond and, therefore, accurate estimates of trisaturate contents were impossible to obtain. For this reason, the method of trisaturate analysis by Iatroscan was used. The results are presented in Table I. It is evident that low linoleate selectivity was accompanied by high trisaturate content. The correlation coefficient was .975.

It is generally understood (5) that catalysts that filter readily have large particle size, small pores and, therefore, low activity. The small pores are likely to increase residence time of the triglycerides and promote trisaturate formation, especially if hydrogen availability is high, i.e., at high hydrogen pressure. It is evident from Table I that the highest trisaturate levels were obtained at high hydrogen pressures.

Dropping points. Dropping points are given in Table I. High dropping points were associated with high trisaturate content. The correlation coefficient was .9404. The reason for the lower correlation coefficient is that triglycerides containing 2 saturated and 1 *trans* fatty acid also have high melting points. In addition, polymorphic form and purity also may influence melting points.

Solid fat content. Figure 3 shows the solid fat content of the oils that were hydrogenated to an iodine value of 65. The solid fat content lines were extrapolated to their respective dropping points. The steepest line represents the oil hydrogenated under the most selective condition of 200 C and 48 kPa, and the flattest line represents the oil hydrogenated under the least selective condition. At about 20 C, all samples contained about the same amount of solid fat. Figure 4 compares the solid fat content of oils hydrogenated under the same condition but with catalyst concentration of 0.1 and 0.2%. Lower catalyst concentration resulted in less selective hydrogenation.

Crystal structure. Because all fats contained about the same amount of solid fat at 20 C, the crystal structure of the samples was examined by X-ray diffraction at 20 C. High trisaturate content corresponded with β crystallinity in the samples (Table I).

Melting curves. Figure 5 shows the melting curves of the hydrogenated samples. Curves 1 and 3 are characterized by sharp peaks of high melting components near the end of the melting curves. Sample 1 contained 14.5% trisaturates and sample 3 had 10.7% trisaturates. The other hydrogenated fats contained less than 5% trisaturates and had relatively flat melting curves.

Pricat 9906 was found to be an active catalyst at high temperature and pressure with lower activity at low temperatures and low pressures. It was found to have excellent filterability properties. It also is a non-selective catalyst that, under certain conditions, may produce relatively large amounts of trisaturates which are undesirable in the manufacture of Canola margarine as they produce β crystallization. Trisaturate content also greatly influences the melting point of fats. Lowering of catalyst concentration promotes non-selectivity. Hydrogenation of oil to a particular iodine value with Pricat 9906 catalyst can result in greatly different solid fat content curves and melting points, due to the amounts of trisaturates formed. It is, therefore, advisable to pay close attention to hydrogenation conditions. Process control by refractive index does not distinguish between the widely different properties of fats with identical iodine values.

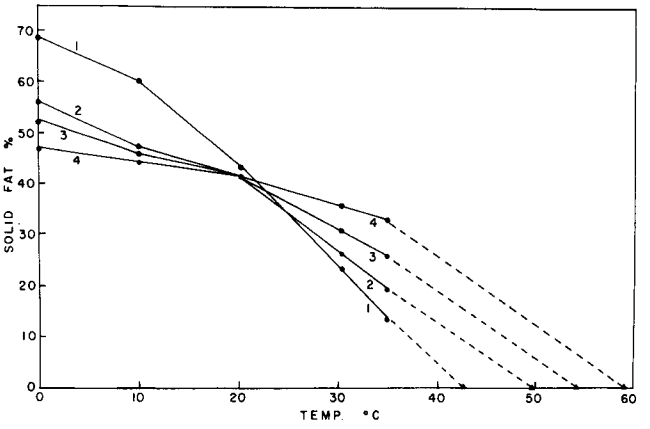

FIG. 3. Plot of solid fat content versus temperature of Canola oil hydrogenated to IV-65 with 0.2% Pricat 9906. Curve 1: 200 C, 48 kPa; Curve 2: 175 C, 138 kPa; Curve 3: 175 C, 276 kPa; Curve 4: 160 C, 276 kPa.

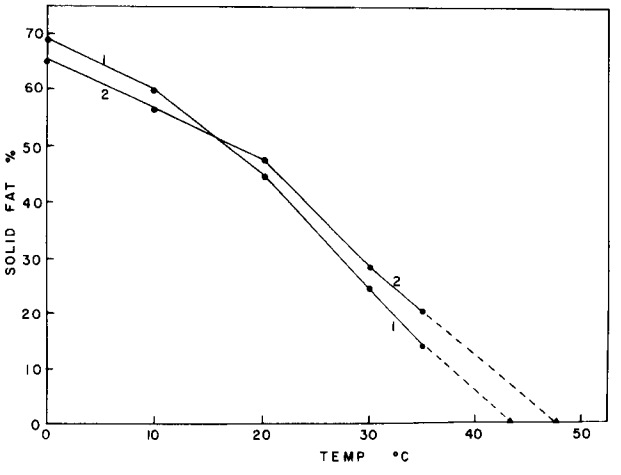

FIG. 4. Plot of solid fat content versus temperature of Canola oil hydrogenated with 0.2% Pricat 9906 (Curve 1) and 0.1% of Pricat 9906 (Curve 2) at 200 C and 48 kPa.

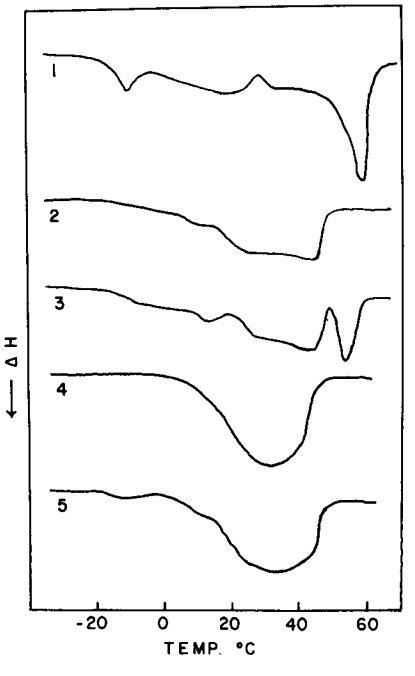

FIG. 5. DSC melting curves of hydrogenated Canola oil (IV-65). Curve 1: 160 C, 276 kPa, 0.2% catalyst; Curve 2: 175 C, 138 kPa, 0.2% catalyst; Curve 3: 175 C, 276 kPa, 0.2% catalyst; Curve 4: 200 C, 48 kPa, 0.2% catalyst; Curve 5: 200 C, 48 kPa, 0.1% catalyst.

The manufacturer recommends multiple reuse of the catalyst. Reuse of the catalyst will result in cost saving and is advantageous for better control over the end product.

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Fatty Acids, Carbohydrates and Crude Protein in Twenty Cassava Cultivars (*Manihot esculenta Crantz*)

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ABSTRACT

Twenty cassava cultivars (*Manihot esculenta* Crantz) were analyzed for fatty acids, nonstructural carbohydrates and crude protein contents. The main constituent fatty acids were myristic, palmitic, stearic, oleic, linoleic and linolenic. Trace amounts of lauric, myristoleic and palmitoleic acids were detected. Saturated acids ranged from 26.58 to 58.05%. Acid-digestible carbohydrates ranged from 11.82 to 40.70% of the green matter. Reducing and non-reducing soluble oligosaccharides also were determined. Crude protein ranged from 1.39 to 4.70% of the dry matter. Linear regression analyses were made, but no significant correlations were found. Some possible genetic relationships are proposed for certain cultivars.

INTRODUCTION

Cassava (*Manihot esculenta* Crantz) tubers contribute a large percentage of the total caloric intake of Brazilian diets (1) and now are used by non-traditional consumers in Japan and China as a complementary source of food (2). In certain cases, such as in Bangladesh, cassava is felt to be a possible solution for basic dietary energy requirements (3).

These observations are due to the fact that cassava is cultivated worldwide. It is grown widely in Northeast Brazil since it is easily adaptable to poor soils and irregular rainfall, and it is economical in terms of both land and labor (4).

Other uses for cassava include the starch industry, cattle feed and alcohol production (5).

Cassava tubers have a basic protein nutrition imbalance in relation to their carbohydrate. Scholz (4) has proposed that the proportion 1:50 represents only 1/10 of the nutritional requirements for a balanced diet. This same author states that two other factors aggravate the problem: lipid imbalance and excessive amounts of fibers in the cassava flour. There are few reports about cassava lipids (6). The reports frequently refer to the ether extract, and as such include not only lipids, but resins, gums, tannins and other compounds extracted from the latex and root skin.

[1] Deceased March 23, 1984.

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Although there are some references to carbohydrates, proteins and total lipids, no report on individual fatty acid analysis was found in the literature (6). The purpose of this study was to make comparative analyses of 20 cassava cultivars for their fatty acids, carbohydrates and crude protein.

MATERIALS AND METHODS

Samples

The analyses were made on lyophilized tubers of 20 cassava cultivars from the germplasm bank of the Universidade Federal de Vicosa, Vicosa, Minas Gerias, Brazil. They were cultivated in a completely randomized experimental design with six replications. The 12-month-old plants included the following cultivars: Sem Nome; Manteigao; SFG 2317; SFG 469; Saracura; Mangue mirim; Mawana; JL-8; Roxinha; Caravela; Prato; Desconhecida; Santinha; Variedate I; Veada; Amargoso; Livoca; Ligeirihna; Gostosa; and Vermelhinha. Normal agricultural practices were used in the field.

Fatty Acids

The lipids were extracted from the lyophilized samples, saponified, methylated according to the technique described by Folchi (7), and then chromatographed on a wall coated, open tubular (WCOT) capillary column (6.0 m × 0.25 mm), covered with diethyleneglycolsuccinate. The temperatures were injector 250 C, detector 280 C and column isothermal 180 C. The apparatus was a Varian 3700 with a DFI detector, DDS-111 processor-integrator and potentiometric recorder Linear model 252 A/M/. The gases were nitrogen (250 ml/min), hydrogen (30 ml/min) and synthetic air (30 ml/min). The quantification was made from peak areas and identification done by comparison with standards.

Crude Protein

Crude protein was determined by the Kjeldahl method modified by Teles for cassava to exclude cyanogenic glycoside interference (8).