Catalytic Carboxylation of Fats: Carboxy Acids from Polyunsaturates[1]

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ABSTRACT

Studies with a palladium chloride-triphenylphosphine catalyst have been extended to the carboxylation of polyunsaturated fats. Linseed, soybean, and safflower oils, acids, and esters were carboxylated catalytically with water-carbon monoxide (4000 psig) at 120-160 C with or without acetone as a solvent. Main products were monocarboxy, 1,3- and 1,4-dicarboxy and tricarboxy acids. Minor products were carbomethoxy esters and disubstituted 2-cyclopentenone. Optimum reaction conditions were determined for the carboxylation of linseed oil and methyl esters by statistically designed experiments. Yields of total carboxy and tricarboxy acids were maximized at low triphenylphosphine and water levels, low temperatures, and high palladium-chloride concentrations. Carboxylated soybean esters were separated by ether extraction of the palladium catalyst from sodium carbonate or hydroxide carboxylate salts. This salt extraction permits catalyst recycling.

INTRODUCTION

The reaction of monoolefins with Pd catalysts and CO produces saturated carboxylic acids with H_2O and carboxylic esters with alcohols (1-4). When this catalytic reaction is applied to polyolefins, the nature of the products is influenced by structure of the substrates and by reaction conditions. Conjugated diolefins produce β-γ-unsaturated esters, whereas nonconjugated diolefins produce mixtures of unsaturated monoesters and saturated diesters (3,4). With $(Bu_3P)_2PdI_2$ in methanol and a CO pressure of 15,000 psig, a cyclic γ-keto ester is formed in 5-10% yield from 1,4-pentadiene and in 40-50% yield from 1,5-hexadiene (5). With $(Ph_3P)_2PdCl_2$ in ethanol-HCl and from 4400-10,000 psig CO, the products from 1,3,5-cyclododecatriene consist of 90% monoester at 35-50 C, 70-80% diester at 50-70 C, and 70-80% triester above 70 C (6).

A highly selective catalyst consisting of a mixture of $PdCl_2$ and Ph_3P was previously described (7) for the carboxylation of oleic acid with CO and H_2O to produce 9(10)-carboxystearic acid in 85-99% yields. A similar catalyst mixture was used with α-olefins in a study (8) aimed at increasing yields of straight chain carboxylic acids useful as surface-active agents. When the $PdCl_2$-Ph_3P catalyst mixture used for oleic acid was applied to linoleic and linolenic acids and esters, the main products were 1,3- and 1,4-dicarboxy and tricarboxy acids (9). Minor products included unsaturated monocarboxy and dicarboxy acids, carbomethoxy esters and the disubstituted α-β-unsaturated cyclic ketones Ia and Ib:
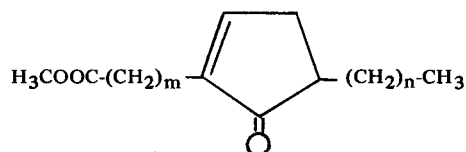
Ia (m, n = 7, 5): 2(5)-hexyl-5(2)-carbomethoxyheptyl-2-cyclopentenone

Ib (m, n = 8,4): 2(5)-pentyl-5(2)-carbomethoxyoctyl-2-cyclopentenone

In this article studies with $PdCl_2$-Ph_3P catalyst mixture have been extended to the carboxylation of polyunsaturated acids, esters, and triglycerides. One practical goal has been to determine process conditions that increase yields of polycarboxylic acids from vegetable oils, since these products hold possible industrial importance.

EXPERIMENTAL PROCEDURES

Materials and Methods

Soybean, linseed, and safflower oils were refined commercially and bleached. Distilled methyl esters were prepared by transesterification and fatty acids by saponification. Fatty acid compositions (by gas liquid chromatography [GLC]) were as follows: soybean oil—9.5% palmitate, 3.7% stearate, 23.5% oleate, 55.6% linoleate, and 7.7% linolenate; linseed oil—6.3% palmitate, 3.3% stearate, 22.0% oleate, 15.1% olinoleate, and 53.3% linolenate; and safflower oil—7.4% palmitate, 1.9% stearate, 12.5% oleate, and 78.2% linoleate. The catalyst components, $PdCl_2$ and Ph_3P, were the same as described previously (7). Methods for GLC, thin layer chromatography (TLC), IR, and mass spectrometry for monocarboxy and polycarboxy acids and esters also have been described previously (10,11).

Carboxylations

The procedure was similar to that reported for monounsaturates (7). Examples of runs made at different scales for polyunsaturated oils, acids, and methyl esters are described here in detail.

Linseed oil (run 1): A 300 ml Hasteloy C stainless steel autoclave was charged under a N_2 blanket with linseed oil (75 g), $PdCl_2$ (0.5 g, 0.5 M %), Ph_3P (3.0 g, 2 M %), distilled H_2O (11.4 g, 10 M % excess), and acetone (75 ml). The autoclave was sealed, purged 3 times with CO and then pressurized with the same gas to 3000 psig. A magnetic stirrer was started, and heat was applied. After 17 min, temperature of the reaction mixture reached 150 C and pressure increased to 4175 psig. The temperature was controlled at 150 C ± 2 C for 4 hr; during this period, the pressure decreased to 3750-3900 and was restored 6 times to 4000 psig. After the autoclave was brought to room temperature, all gases were vented, and the contents were transferred with acetone and filtered as before (7). The greenish-orange crude product (84.3 g) was analyzed directly by titration (acid value: 224) and after saponification and methylation (diazomethane) by GLC (9.4% saturates [sat], 1.4% unsaturates [un], 22.7% monocarboxy acids [mono], 26.6% dicarboxy acids [di], 29.5% tricarboxy acids [tri] and 10.4% keto). A large sample (32.5 g) was transmethylated by refluxing with CH_3OH (96 g) and concentrated H_2SO_4 (0.8 g) for 24 hr. Distillation of methyl esters (31.8 g) yielded fractions in which mono-, di-, and tricarboxy acids are concentrated (Table I).

Linseed acids (run 2): Distilled linseed fatty acids (100 g) were hydrocarboxylated as in run 1 with 0.67 g $PdCl_2$ (0.5 M %), 3.99 g Ph_3P (2 M %), 13.45 g H_2O (10 M % excess), and 50 ml acetone. This reaction required 6 hr at 150 C and 4000 psig CO to reach completion. The crude yellow product (106.2 g) was analyzed by titration (acid value: 299) and GLC after methylation with diazomethane (11.7% sat, 9.5% un, 37.6% mono, 26.1% di, 10.8% tri, and 4.3% keto). Distillation data on methyl ester derivatives are given in Table I.

TABLE I

Separation and Fractionation of Carboxylated Products

Run no.	Starting materials[a]	Methods of separation[b]	Fraction	Temperature (C)	Yield (%)	GLC analysis[c] (%)				Carboxy acids			
						Pal	St	Un	Keto	Mono	Di	Tri	Total
1	LSO	Pot distillation (Vigreux column, 0.01-0.015 mm)	1	120-140	6.9	67.3	19.6	3.3		9.8			9.8
			2	140-165	23.1	2.1	12.0	2.7	3.0	71.2	7.7	1.3	80.2
			3	181-197	13.8				10.7	44.7	33.6	11.0	89.3
			4	198-211	15.5				9.8	2.6	62.4	25.2	90.2
			5	211-225	19.0				1.8		37.2	61.0	98.2
			6	225-250	7.6						3.3	96.7	100
2	LS acids	Alembic distillation (0.01 mm)	1	100-123	10.0	46.2	22.4	2.5	5.8	18.7	4.4		23.1
			2	130-138	30.6	0.3	3.6		16.3	52.0	20.2	7.6	79.8
			3	138-148	27.2				6.6	2.9	51.4	39.1	93.4
			4	148-176	25.7						7.6	92.4	100
3[d]	MeSBO	Molecular distillation (0.002 mm)		200-207	72.0	14.1	7.7		5.7	34.8	36.9	0.8	72.5
		Na2CO3 salt extraction			71.1	4.2	2.6			29.1	54.8	9.3	93.2
		NaOH salt extraction	1		74.0	5.4	2.9	0.4		30.4	53.2	7.7	91.3
		Ether extract	2		20.3	31.0	14.8	1.1	25.3	15.2	12.6[e]		
	Ether extract	Pot distillation (short path 0.01 mm)	1	110-136	35.3	66.0	31.5	2.5					
			2	136-145	9.6	31.6	42.4	2.6	14.9	8.5			
			3	145-168	22.1	1.8	23.0	2.2	31.8	36.5	4.7[e]		
			4	168-185	25.0	0.6	1.7	1.7	42.8	24.0	29.2[e]		
4	MeLSO	NaOH salt extraction	1		80.3	2.5	1.4			23.7	29.0	43.4	96.1
		Ether extract	2		16.1	20.6	15.1	0.6	29.1	26.7	7.9[e]		

[a]LSO = linseed oil, LS = linseed, MeSBO = soybean methyl esters.

[b]On methyl esters.

[c]By gas liquid chromatography (GLC) analysis of methyl esters on JXR column (12); Pal = palmitate, St = stearate, and Un = unsaturates.

[d]See "Experimental Procedures".

[e]Dicarboxy acids plus unidentified polar material of same retention.

[f]GLC analysis: 8.8% sat, 17.4% mono, 23.4% di, 43.6% tri, and 6.6% keto.

Soybean methyl esters (run 3): The esters (802 g) were hydrocarboxylated in a 2 liter Hasteloy C stainless steel rocker-shaker autoclave by the same procedure as for the linseed oil, but no acetone solvent was used. The reactants included 3.5 g $PdCl_2$ (0.5 M %), 21 g Ph_3P (2 M %), and 80 g distilled H_2O (10 M % excess). The reaction required 5.5 hr at 150 C and 3900-400 psig CO to reach completion. Filtration of the dark amber crude product (971 g) yielded 5.6 g crystalline brown precipitate. Another brown precipitate (5.2 g) was formed from the crude product. These precipitates were used subsequently in catalyst recycling experiments. The crude product was analyzed by titration (acid value: 182) and by GLC after methylation with diazomethane (18.3% sat, 27.8% mono, 44.0% di, 6.0% tri, and 3.9% keto).

Separations

Carboxylated fatty esters were separated from the Pd complex catalyst by either molecular distillation (Rota-Film, A.F. Smith, Pompano Beach, Fla.) or by ether extraction of the carboxylate salts obtained with sodium carbonate (13) or sodium hydroxide. Salt extraction affords more concentrated carboxy acids than does molecular distillation (Table I). The two salt extraction procedures are described in detail, because they provide an approach to a catalytic recycling process.

Sodium carbonate carboxylate salt extraction: To a suspension of carboxylated soybean esters (100 g, run 3, Table I) in 100 ml water, 30 g Na_2CO_3 was added carefully and in small portions allowing for CO_2 to evolve. The salt solution then was extracted 3 times with 100 ml petroleum ether. Each petroleum ether extract was washed with 10% aqueous Na_2CO_3.

The combined carboxylate salt solution was acidified carefully with dilute HCl, again allowing CO_2 to evolve. The acidified solution of carboxylated esters was extracted with petroleum ether and diethyl ether and dried over Na_2SO_4. The solvent was distilled off with a rotating evaporator under vacuum (yield: 71.1 g; acid value: 233).

The petroleum ether extracts of the salts (containing Pd)

were washed with water to neutrality and dried (Na_2SO_4). Removal of the solvent gave a dark brown oil containing the Pd catalyst (yield: 21.5 g; acid value: 2.8). This oily extract was first distilled (100-160 C/0.01 mm), and the Pd catalyst was concentrated in the residue (3.25% by wt). The distillate then was redistilled into fractions containing various concentrations of fatty esters, mono- and dicarboxy esters, cyclic keto, and unidentified polar compounds (Table I).

Sodium hydroxide carboxylate salt extraction: An aqueous NaOH solution was added slowly to a stirred mixture of 100 g crude carboxylated soybean esters (run 3, Table I) and 100 ml water until the pH was 11-12 (15 g NaOH required). The carboxylate salt solution was extracted 4 times with petroleum ether, and each extract was in turn washed with 10% aqueous NaOH. The combined carboxylate salt and NaOH washes were acidified carefully with concentrated HCl to pH 2. The petroleum ether extracts were isolated as described above for the Na_2CO_3 salt procedure. Yield and analytical data are given in Table I.

RESULTS

Linseed, soybean, and safflower oils; their methyl esters; and fatty acids were carboxylated with a $PdCl_2$-Ph_3P catalyst mixture, CO and H_2O under various conditions. The products were analyzed by GLC and acid values. Most or all of the unsaturation in the substrates studied was converted into a mixture of mono-, di-, and tricarboxy acids totaling 52-85%. Main products from linseed oil and its derivatives included 15-38% mono-, 23-32% di-, and 11-47% tricarboxy acids. Products from soybean oil and its derivatives consisted of 28-31% mono-, 26-44% di-, and 2-6% tricarboxy acids. Products from safflower oil and acids included 22-33% mono- and 43-61% dicarboxy acids. Nonacidic by-products comprised 4-16% cyclic ketones. Although most runs were made in acetone solution, the results were similar in the absence of solvent. Yields of carboxy acids were lower in acetic acid than in acetone solvent.

Runs with linseed oil and linseed methyl esters were analyzed statistically (14) to test the effect of several fac-

tors upon carboxylation product distribution. Table II shows the means for levels of factors computed on measurements from 21 runs. Also shown is the least significant difference (95% level) for comparing means based upon various numbers of runs. The F ratios for testing statistical significance were computed from the pool variance s^2 (s is the standard deviation) derived from duplicate runs and the analysis of variance.

For the linseed oil runs, water at a high level had a most significant effect in decreasing tricarboxy acids and GLC acid values, as well as catalyst activity (longer reaction times). High catalyst concentration (at a constant $Ph_3:PdCl_2$ ratio of 4) significantly increased tricarboxy and acid values and decreased dicarboxy acids. Temperature changes between 140-150 C had no significant effect. For the linseed ester runs, higher temperatures and water levels decreased yields of tricarboxy acids and GLC acid values and increased yields of dicarboxy acids and cyclic ketones.

No significant interaction effects were observed with linseed methyl esters. With linseed oil significant interactions influenced the yield of tricarboxy acids and GLC acid values. Yields of tricarboxy acids increased with temperature at high water and low catalyst levels and increased with catalyst concentration at high water. The combination of low catalyst level and high water level was especially unfavorable. GLC acid values followed practically the same pattern. Evidently, tricarboxy acid yields from both linseed oils and methyl esters are maximized at low water and Ph_3P levels and low temperatures but at high $PdCl_2$ concentrations.

Carboxy acids concentrated by salt extraction and by distillation (Table I) were separated by silicic acid column chromatography (10) after methylation with diazomethane. Functional characterization was based upon elemental analysis (Table III) and comparison of chromatographic behavior (GLC and TLC), IR and NMR spectra with corresponding hydroformylation, and hydrocarboxylation derivatives from oleate (7,12) and from linoleate and linolenate (9,11). The same chromatographic system further fractionated the neutral ether extracts of the salts from carboxylated soybean esters (Table III). Monocarbomethoxy esters and cyclic ketones were eluted successively with 5:95 and 10:90 diethyl ether: petroleum ether mixtures. The ketone fraction had the same chromatographic properties (GLC and TLC), IR (bands at 1700 and 1630 cm^{-1} for C=C-C=O), NMR (band at 7.09 ppm for olefin ring H in cyclopentenone), UV (maximum at 222 nm for C=C-C=O), and mass spectra (m/e 322: M, molecular ion; m/e 291: M - OCH_3) as the corresponding cyclic ketone from pure methyl linoleate (9). Isomeric mass spectral analysis showed this ketone to be a mixture of Ia and Ib.

Further identification of carboxy esters was achieved by mass spectral studies. Characteristic fragment of the mono-

TABLE II

Three Way Analysis of Variance—Mean Values for Various Levels[a]

Factor	Level	Carboxy acids (%)			Percent keto	GLC acid value
		Mono	Di	Tri		
Carboxylated Linseed Oil						
W	10	24.4	26.1	29.3	9.5	211
	100	27.0	27.3	23.6**	7.6	198**
T	140	24.2	27.0	26.0	9.4	201
	150	27.2	26.4	27.0	7.7	208*
C	0.5	24.2	29.0	22.6	9.4	195
	1.0	27.1	24.4*	30.4**	7.7	214**
	LSD	3.7	1.4	1.9	2.1	5.7
Carboxylated Linseed Methyl Esters						
P	1	17.6	26.5	38.0	7.2	231
	2	18.7	25.9	38.0	8.2*	230
	4	19.9	25.8	34.3*	9.9*	218*
	LSD	3.7	1.4	1.9	2.1	5.7
T	130	16.9	25.3	40.6	7.4	233
	150	20.5*	26.8*	33.0**	9.4*	219*
	LSD	3.0	1.1	1.5	1.7	4.6
W	10	18.8	23.4	40.1	7.6	230
	100	18.7	28.7**	33.4**	9.2*	223*
	LSD	3.0	1.1	1.5	1.7	4.6
	s	1.86	0.69	0.95	1.1	2.9

[a]W = water, M % excess; T = temperature, C; C = catalyst, M % $PdCl_2$ + Ph_3P (1:4); P = Ph_3P, M %. LSD = least significant difference (95% level); s = standard deviation; * = differences significant at 5% level based upon calculated F ratio; ** = significant at 1% level.

carboxy acid fraction from carboxylated linseed methyl esters (run 4, Table I) included (m/e, relative intensity): M - OCH_3 (325, 10.32), M - $COOCH_3$ + H (297, 18.84), M - CH_2COOCH_3 (283, 12.54); of the *dicarboxy acid* fraction: M (414, 0.49), M - OCH_3 + H (383, 28.81), M - $COOCH_3$ - H (354, 11.23), M - $COOCH_3$ - OCH_3 (323, 14.29), 1,4-diester (174, 25.58), 1,3-diester (160, 41.21); and of the *tricarboxy acid* fraction: M (472, 0.56), M - OCH_3 (441, 28.11), M - OCH_3 - OCH_3 - H (409, 8.70), 1,4-diester (174, 18.60), 1,3-diester (160, 39.30). Isomeric composition, calculated on the basis of previous mass spectral studies (10,11), is given in Figure 1. The carbomethoxystearates from linseed esters have the carboxy acid branch located mainly on C-9 and C-10 (71%). The remaining monocarboxy acid isomers are distributed between C-8 to C-16, with a maximum at C-11. The dicarbomethoxystearates consist of 62% 1,3-isomers (mainly 8,10-, 10, 12-, and 11,13-) and 38% 1,4-isomers (mainly 9,12- and 10,13-). In agreement with previous results (9), the isomeric distribution of carboxy acids indicates that polycarboxylation is accompanied by significant double bond isomerization. Catalytic conjugation of the polyunsaturates under CO pressure would account for the greater concentrations of

TABLE III

Chromatographic Fractions[a] from Carboxylated Polyunsaturates

Starting materials[b]	Solvent,[c] % EE/PE	Characterization (GLC,[d] TLC)	Purity (GLC)[d]	Carbon (%)		Hydrogen (%)	
				Calculated[e]	Found	Calculated[e]	Found
M₉LSO salts	15/85	Carbomethoxystearate	95.1	70.74	71.20	11.31	11.59
	15/85	Dicarbomethoxystearate	93.1	66.63	67.41	10.21	10.37
	25/75	Tricarbomethoxystearate	98.0	63.53	63.48	9.38	9.18
LS acids distillation	5/95	Carbomethoxystearate	99.0	70.74	70.97	11.31	11.51
fraction 2	15/85	Dicarbomethoxystearate	97.0	66.63	67.51	10.21	10.40
MeSBO-ether extract	10/90	Cyclic ketone Ia,b	97.2	74.49	73.88	10.63	10.75

[a]Silicic acid column chromatography (10)

[b]See Table I.

[c]EE = diethyl ether; PE = petroleum ether.

[d]See footnote c, Table I. GLC = Gas liquid chromatography, and TLC = thin layer chromatography.

[e]Methyl carbomethoxystearate, $C_{21}H_{40}O_4$; methyl dicarbomethoxystearate, $C_{23}H_{42}O_6$; methyl tricarbomethoxystearate, $C_{25}H_{44}O_8$; and keto Ia,b, $C_{20}H_{34}O_3$.
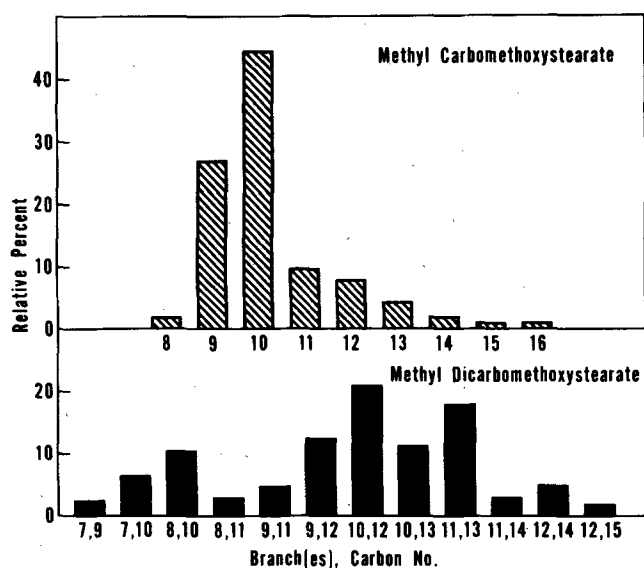
FIG. 1. Distribution of isomeric methyl carbomethoxy- and methyl dicarbomethoxystearates from linseed esters hydrocarboxylated with palladium chloride-triphenylphosphine catalyst (run 4, Table I).

1,3- than 1,4-dicarboxy acids in carboxylated linseed esters (Fig. 1).

Activity of the used Pd catalyst was examined as an approach to a recycle carboxylation process. Distilling the neutral ether extract from salts of carboxylated soybean methyl esters (Table I) concentrates used Pd catalyst in the pot residue. This residue was used as a catalyst at a concentration based upon recovered wt. With added HCl and Ph_3P, it proved to be as active as fresh $PdCl_2$ for the carboxylation of soybean methyl esters (Table IV). In another experiment, Ph_3P was replaced with the precipitates isolated by filtration of the crude carboxylated soybean esters ("Experimental Procedures"). In this experiment, the carboxy acids produced after 6 hr totaled 78%, compared to 83% when Ph_3P was added. Apparently, the salt extraction procedure used to concentrate the carboxy acids would provide also the basis for a catalytic recycling process.

DISCUSSION

In a previous study (9), we demonstrated that the hydrocarboxylation of linoleic and linolenic acids catalyzed by $PdCl_2$-Ph_3P is more complex than that of oleate, because there is significant double bond isomerization, some hydrogenation, and cyclic ketone formation. In the present study with linseed esters, we found that the amounts of H_2O and Ph_3P, as well as the temperature, are important variables that influence both yields of tricarboxy acid and the weighted total, as measured by GLC acid values. The negative effect of high H_2O levels may arise, because a heterogeneous reaction mixture is formed. Phase separation was, indeed, observed during sampling of some reaction mixtures run at high H_2O levels. High levels of Ph_3P lowered GLC acid values and yields of tricarboxy acids. The negative effect of temperature upon yields of total and tricarboxy acids may be attributed to increased conjugation of polyunsaturates. Conjugation would decrease polycarboxylation, because 1,3-dienes are more difficult to react with CO than are 1,4-dienes (9).

The isomeric distribution of monocarboxy acids of linseed esters is in marked contrast to those of pure linoleate and linolenate. The monocarboxy acids have their carboxy branch located mainly on C-10 and C-12 in carboxylated linoleate and mainly on C-10 and C-15 in carboxylated

linolenate (9), whereas in carboxylated linseed esters it is mainly on C-9 and C-10. The isomeric carboxy product from linseed esters (Fig. 1) suggests that with mixtures of polyunsaturated fatty esters, hydrocarboxylation is stepwise. Monocarboxylation would occur mainly at C-9 and C-10 positions and dicarboxylation between C-8 and C-13 positions. Although the tricarboxy acids of linolenate and linseed esters were not well identified, tricarboxylation would occur presumably at the remaining C-15 and C-16 positions. A similar explanation was suggested for the stepwise hydroformylation of linseed esters (15). The catalytic carboxylation of pure linolenate involves also the stepwise formation of carboxyoleate, carboxylinoleate, and dicarboxyoleate (9).

Areas of applications for the C_{19} hydroformylation and carboxylation products of oleate include lubricants, plasticizers, polyurethanes, coatings, and polyamide resins (16). The corresponding carboxylation products and derivatives of polyunsaturated vegetable oils also are finding many uses which will be reported later.

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