Some Esters of Mono-, Di-, and Tricarboxystearic Acid as Plasticizers: Preparation and Evaluation

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ABSTRACT

Methyl mono-,di-, and tricarboxystearates were prepared by either a two-step hydroformylation-oxidation reaction or direct hydrocarboxylation of unsaturated vegetable oil methyl esters. Procedures were developed for preparing alkyl dicarbomethoxy-, dicarboethoxy-, and dicarbobutoxystearates. These triesters, along with some di- and tetraesters from mono- and tricarboxystearic acids, were evaluated as primary plasticizers for polyvinyl chloride (PVC). Except for butyl carbobutoxystearate, the esters were compatible at the 32% level and had properties equal or superior to those of dioctyl phthalate. Methyl and butyl diesters of carboxystearic acid had undesirable migration and volatility properties. The migration and volatility properties of some tri- and tetraalkyl esters were equal to or better than the controls. Of the various esters tested, methyl dicarbomethoxystearate containing 13-49% methyl tricarbomethoxystearate was an efficient plasticizer for PVC at the 32% level.

INTRODUCTION

Some plasticizers for polyvinyl chloride (PVC), such as di-2-ethylhexyl phthalate (DOP) and sebacate (DOS), no longer meet the requirements of industry. For example, because DOP tends to fog windshields, the auto industry is reluctant to or no longer uses DOP as the plasticizer for vinyl interiors (1). In other applications, the use of DOP is seriously being questioned. For example, lipids present in food and blood stored in PVC containers, bags, and dispensers equipped with plastic tubing leach or extract the DOP plasticizer. Ingested DOP is reported by Jaeger and Rubin (2) to be accumulated and deposited unchanged in human liver tissues. Small quantities of various phthalates have been reported in animal tissues, and numerous abnormalities in several animal species are said to be caused by various phthalate esters (3-5); however, biological implications are still being questioned (6).

Possibly, plasticizers derived from vegetable oils that have low volatility and migration would eliminate some of the difficulties presently encountered with DOP. For example, methyl mono-, di-, and tricarboxystearates (MeCS, MeDiCS, and MeTriCS, respectively) have been made available by selective hydroformylation (7-9) and oxidation (10) processes carried out on vegetable oils containing oleate, linoleate, and linolenate. Mixtures of these acids are also produced by hydrocarboxylation of unsaturated fatty compounds (10,11). Esterification of these methyl carboxystearates by various procedures has produced some new di-, tri-, and tetraalkyl esters. This article reports the preparation and evaluation of these esters as possible plasticizers for PVC.

RESULTS AND DISCUSSION

The complex esters derived from mono-, di-, and tricarboxystearic acid (CSA, DiCSA, and TriCSA) will be abbreviated. The terminal alkyl ester will be named first, followed by the branched ester group or groups; for example, butyl dicarbomethoxystearate becomes Bu-DiMe triester.

Di-, Tri-, and Tetraesters

For plasticizer evaluation, pure alkyl stearates (95+%) with one, two, and three internal carboalkoxy groups were prepared either by a two-step hydroformylation-oxidation reaction (7-9) or by direct hydrocarboxylation of vegetable oil methyl esters (11,12) followed by direct sulfuric acid-catalyzed esterification and/or transesterification procedures previously reported (10,13).

Relatively pure MeCS, MeDiCS, and MeTriCS for the preparation of esters for evaluation were isolated from oxidized-hydroformylated olive, soybean, safflower, and linseed methyl esters (10) by use of either sodium hydroxide or bicarbonate. Products extracted from soybean ester acids with both hydroxide (part 1) and bicarbonate (part 2) are listed in Table I, and extraction of safflower ester acids with sodium hydroxide is given in Table II. By limiting the amount of hydroxide or bicarbonate for extraction of methyl soybean acids, mono-, di-, and tricarboxy methyl stearates were isolated.

For example, a mixture of methyl soybean carboxystearates containing 6.9% MeTriCS when extracted with 5% sodium hydroxide (Table I, fraction 1) or aqueous sodium bicarbonate (Table I, fraction 1) yields relatively pure MeTriCS. Extraction with bicarbonate removes only di- and triacids. The remaining monoacid MeCS must be removed by extraction with sodium hydroxide. Unidentified oxidation by-products, possibly methyl formyloxycarboxy and *bis*(formyloxy)stearate (same gas-liquid chromatographic retention as MeDiCS) and similar to methyl formyloxystearate identified by Friedrich (14), are then concentrated in fractions 6 and 7. Some fractions contained from 6 to 7% nonacidic products, such as methyl palmitate and stearate. These products can be removed from the aqueous organic salt solution by further extraction with ether or hexane.

Roe et al. (15) selectively saponified dialkyl esters of CSA (Koch process) to obtain various methyl-branched carboalkoxystearic acids. In a kinetic study of esterification rates for 9(10)-CSA, Dufek et al. (13) reported that the terminal carboxyl group is ca. 26-27 times more reactive than the internal or branched carboxyl group. Because of this difference in reactivity, diesters of CSA with two different alkyl groups could be prepared by selective alkaline transesterification (10). For example, Me-Me diester when treated with dimethylpentanol (Dmp-OH) or ethylhexanol (EtHex-OH) gave Dmp-Me and EtHex-Me diesters.

The increased reactivity of the terminal carboxyl group over the branched group was utilized also to prepare some new mixed alkyl triesters. Selective saponification of Me-DiMe and Et-DiEt triesters with only the theoretical amount of alkali gave dicarbomethoxy- and dicarboethoxystearic acid (DiMeSA and DiEtSA). Direct sulfuric acid-catalyzed esterification of DiMeSA and DiEtSA with various alcohols yielded alkyl-DiMe and alkyl-DiEt Triesters (Table III).

To identify esters by gas-liquid chromatography (GLC), authentic samples of Bu-DiMe and Me-DiBu triesters were prepared by the following reaction sequence: 1) hydroformylation of safflower butyl esters; 2) oxidation with potassium permanganate; 3) extration with sodium bicarbonate; 4) carboxylic acid chlorination with phosphorus

TABLE I

Extraction of Oxidized-Hydroformylated Soybean Methyl Esters[a]

					Analysis[b] (%)				
Fraction	Reagent (ml)	(pH)	Yield (g)	(NE)	P	S	MeCS	MeDiCS	MeTriCS
Oxidized-hydroformylated esters			992	294.0	11.1	6.0	29.4[c]	43.6	6.9
			480g with 5% sodium hydroxide						
1	300	7.2	21.0	154.9	Trace	0.3	Trace	16.7	81.4
2	300; 80 ml MeOH	7.6	117.8	203.1	0.6	0.6	3.1	88.0	7.7
3	300	8.9	110.5	241.3	1.2	2.6	14.3	79.5	---
4	50	9.7	24.8	344.6	2.2	4.3	62.7	30.8	---
5	50	10.0	11.7	352.6	0.7	2.2	74.3	21.3	---
6	200	12.8	90.5	280.9	0.2	0.4	87.3	11.8	---
7	Neutrals		94.8	[d]	34.0	24.4	26.3[e]	11.5[f]	---
		Total	471.1						
			480g with bicarbonate						
1	250 ml 10% $NaHCO_3$	7.3	17.2	150.2	Trace	0.3	0.5	7.5	87.8
2	250 ml 10% $KHCO_3$, 80 ml MeOH	7.6	42.1	193.5	Trace	Trace	1.0	80.0	15.8
3	250 ml 10% $KHCO_3$, 80 ml MeOH	7.9	41.7	199.8	Trace	Trace	1.4	90.0	7.2
4	250 ml 10% $KHCO_3$, 80 ml MeOH		87.9	210.9	0.7	0.8	4.7	93.5	---
5	250 ml 10% $KHCO_3$, 80 ml MeOH	8.4	22.5	208.7	0.4	0.4	2.2	92.6	---
6	5% NaOH to pH	11.8	137.4	355.0	2.3	3.4	65.5	27.0[g]	---
7	Neutrals[h]		126.9	[i]	23.2	19.2	20.3	13.2[f]	---
		Total	475.7						

[a] Abbreviations: NE = neutral equivalent, P = methyl palmitate, S = methyl stearate, MeCS = methyl monocarboxystearate, MeDiCS = methyl dicarboxystearate, MeTriCS = methyl tricarboxystearate.

[b] Plus short chain and trace amounts of unidentified products to total 100%.

[c] Includes 4.4% methyl formyloxystearate (14).

[d] Calcd as 2.1% MeCS.

[e] Includes 23.0% methyl formyl- and/or formyloxystearate.

[f] Unidentified disubstituted products such as methyl *bis*(formyloxy)stearate.

[g] May contain methyl formyloxycarboxystearate.

[h] Also contains 18.4% methyl hydroxy-, keto-, and formyloxystearate.

[i] Calcd as 19.2% MeCS.

TABLE II

Alkali Extraction of Oxidized-Hydroformylated Safflower Methyl Esters

Fraction	5% NaOH (ml)	Yield[a] (g)	MeCS[b] (%)	MeDiCS[b] (%)
1	800	35.8	1.3	95.0[c]
2	800	403.5	2.8	92.7[c]
3	400	114.1	2.1	94.8[c]
4	300	96.1	19.7	62.5
5	800	212.6	57.1	27.5
6	800	3.4	---	---
7	Neutrals in ether	195.2		

[a] After acidification. Yield from oxidation of 996 g of hydroformylated safflower methyl esters.

[b] MeCS = methyl monocarboxystearate, MeDiCS = methyl dicarboxystearate. Plus short chain and trace products to make 100%.

[c] Fractions 1-3 were combined and used to prepare triesters listed in Table III. The neutral equivalent was 203. Calcd 193.

trichloride; and 5) esterification of butyl *bis*(chlorocarbonyl)stearate with methanol containing pyridine (13). Me-DiBu triester was prepared similarly from Me-DiCS and *n*-butyl alcohol. These pure esters (95% or better), as well as the ester mixtures prepared by hydrocarboxylation, were evaluated as plasticizers (Table IV).

Alkali extraction, esterification, and distillation (or distillation followed by esterification) of the carboxylic acid products from direct hydrocarboxylation of soybean and linseed methyl esters gave mixtures of alkyl mono-, di-, and tricarboalkoxystearates. The composition of these esters is shown in Table IV under hydrocarboxylated samples (Nos. 17-23). The main products characterized by mass spectrometry were 1,3- and 1,4-dicarboalkoxy esters relative to each other from hydrocarboxylation of methyl linoleate and tricarboalkoxy esters from methyl linolenate (16). The 1,4-disubstituted carboalkoxy esters predominated in the oxidized-hydroformylated polyunsaturates (9). Since the starting materials for these products were methyl esters and since no attempts were made to remove methanol completely during transesterification-esterification with butanol, the hydrocarboxylated products (Table IV, Nos. 19, 20, 22, and 23) may contain methyl esters. Identification of this mixture of methyl and butyl carbomethoxy and butoxy esters by GLC was only tentative. The retention times were intermediate between the known retention times for the all-methyl and all-butyl esters.

Plasticizer Evaluation

As plasticizers, all the alkyl and mixed alkyl esters of CSA, DiCSA, and TriCSA, except Bu-Bu diesters, had properties equal to or better than those of the controls.

Compatibility of the plasticizers was good, except for the two Bu-Bu diesters (Nos. 4 and 5), which exuded from PVC after 24 hr (Table IV). For the remaining samples, which did not exude, relative degrees of compatibility can be judged by use of compatibility numbers and by their plot against T_f (Fig. 1). Compatiblity number (Δ) is defined by Riser and Palm (17) as the difference between T_f and T_4, which in turn are defined as the temperature at the respective elasticity moduli of 135,000 and 10,000 psi (18).

TABLE III

Alkyl Dicarboalkoxystearates

Alkyl	Alkoxy	Boiling point[a] (C at mm)	n_D^{20}	d_4^{20}	Carbon (%)		Hydrogen (%)	
					Calcd	Found	Calcd	Found
Methyl	Methyl	195-200 0.1	1.4524	0.9952	66.63	66.31	10.21	9.85
Ethyl	Methyl	220-225 0.1	1.4510	0.9846	67.25	67.05	10.35	10.46
Isopropyl	Methyl	220-225 0.1	1.4500	0.9731	67.83	67.72	10.48	10.53
n-Butyl	Methyl	270-275 0.5	1.4520	0.9700	68.38	68.40	10.62	10.30
2-Ethylhexyl	Methyl	250-255 0.07	1.4538	0.9493	70.21	70.01	11.01	11.11
2,2-Dimethylpentyl	Methyl	260-265 0.1	1.4547	0.9624	69.84	69.33	10.93	10.80
Methyl	Ethyl	215-218 0.1	1.4503	0.9716	67.83	67.84	10.48	10.67
Ethyl	Ethyl	220-225 0.1	1.4495	0.9641	68.38	68.60	10.59	10.33
n-Butyl	Ethyl	248-253 0.1	1.4505	0.9565	69.38	70.21	10.81	10.86
2-Ethylhexyl	Ethyl	250-258 0.1	1.4524	0.9394	71.07	71.01	11.18	11.17
Methyl	*n*-Butyl	207-210 0.025[b]	1.4509	0.9558	69.84	70.45	10.91	11.08

[a] Distillation through a falling film still.

[b] Pot distillation.

A straight-line plot of flex temperatures T_f vs. Δ is drawn for three widely used commercial plasticizers: tricresyl phosphate (TCP), DOP, and bis(2-ethylhexyl) azelate (DOZ). Plasticizers with low compatibility values (Δ), which fall to the left of the straight-line plot, are efficient and compatible with PVC. The values for the carboxystearate samples are plotted in Figure 1. Thus, almost all esters listed in Table IV, except Bu-Bu diesters (Nos. 4,5) and possibly EtHex-DiEt triester (No. 16), are compatible. The compatibility values for five additional esters fall to the right and close to the straight-line plot. These values, however, are considered to be within experimental error. The Bu-Bu diester (No. 5) prepared from commercially available CSA that has a large number of isomers in other than the 9,10-position had an extremely high Δ value of 69. A lower but still unacceptable Δ value of 63 was obtained for the Bu-9(10)-Bu diester (No. 4) prepared by selective hydroformylation with rhodium catalyst. Both Bu-Bu diesters exudated after 24 hr. As reported by Roe et al. (15), these results were not entirely unexpected, since a ratio of 12 carbon atoms to one ester linkage is generally accepted as the maximum for compatibility. The Bu-Bu diester has a ratio of 27:2.

Mixed diesters prepared by esterification of a diacid with a mixture of two alcohols have lower flex temperatures (19). The flex temperatures of the mixed alkyl triesters (alkyl DiMe and alkyl DiEt triesters) are 5-10 C lower than the DOP controls, but little or no difference is noted when the mixed esters are compared with homogenous alkyl triesters, such as Me-DiMe and Et-DiEt triesters. There is, however, a noticeable lowering of T_f when the size of the alkyl group in the internal ester is increased. For example, the T_f for the alkyl DiEt triesters (Nos. 13-16) are 5-6 C lower than the corresponding alkyl DiMe triesters (Nos. 8-12). An increase in the size of the internal ester group from Bu-DiEt (No. 15; $T_f = -39$ C) to Bu-DiBu (No. 6; $T_f = -40$ C) does not produce a further lowering of T_f. Thus, for mixed triesters of DiCSA, the T_f apparently reaches the optimum low temperature ca. -40 C. Changing the internal ester group to larger alkyl, such as in alkyl-DiEtHex triester, probably would raise the T_f.

Increasing the number of internal ester groups drastically increases T_f; for example, butyl esters of mono-, di-, and tricarboxystearic acid (Nos. 5-7). The T_f is raised from -58 to -40 to -28 C by additional internal carbobutoxy groups. Little or no difference in T_f is noted between samples with varied positional isomers. Bu 9(10)-Bu diester (No. 4), prepared from methyl oleate by selective hydroformylation, had a T_f of -57 C, and the Bu-Bu diester mixture (No. 5) containing isomers additional to the 9(10)-isomer had a T_f of -58 C.

For permanance, plasticizers ideally should have a low tendency to migrate, but as a group alkyl-dialkyl triesters (Nos. 8-16) had rather high values of 8-11%. Dmp-DiMe triester (no. 12) with 5.5% migration was the only exception. Migration loss of 5.4% for Bu-TriBu tetraester (No. 7) prepared via hydroformylation reactions compared favorably with 4.1 and 3.9% for DOP and Plastolein controls and also was excellent when compared with 19.3% for DOS. The sample containing equal amounts (49.4%) of Me-DiMe and Me-TriMe esters (No. 21) prepared by direct hydrocarboxylation had the lowest migration value of 3.4%. Migration is affected somewhat by volatility. Generally, boiling points above 200 C at 4 mm of pressure are required for efficient plasticizers. All esters in Table IV meet these requirements. Volatility wt loss of 0.6-0.8% for several samples is lower than that of the three controls.

Heat stability for samples prepared by the two-step hydroformylation-oxidation reaction is somewhat lower than that of the controls. There is, however, a noticeable decrease in heat stability for the esters prepared by direct hydrocarboxylation. Unfortunately, two different lots of commercial PVC resin (Geon 101 and Geon 102EP) were used for this study. Heat stability for samples prepared with Geon 102EP is greater than that of samples prepared with Geon 101, as shown for the two DOP controls. Consequently, the higher heat stability values for samples 8-16 are also attributed to Geon 102EP.

High flexibility, tensile strength, and elongation of PVC sheets are desirable; although values for PVC sheets plasticized with various alkyl carboalkoxystearates vary, they essentially are equivalent to the controls. Me-DiMe triester containing 13, 20, and 49% Me-TriMe tetraester (Nos. 2,18,21) exceeded tensile strength, 100% modulus, and elongation of PVC plasticized with DOP, and these three mixtures are considered to be very efficient plasticizers.

EXPERIMENTAL PROCEDURES

Samples (ca. 1 mg) were treated with diazomethane and analyzed by GLC programmed from 180 to 300 C at 2 or 4 C/min, 30 cc/min on a F&M Model 5750 instrument equipped with a 6 ft x 1/4 in. 3% JXR column.

Methyl Carboxystearate (MeCS) and Methyl Tricarboxystearate (MeTriCS)

Olive and linseed methyl esters were hydroformylated, oxidized, and extracted with either sodium hydroxide or potassium bicarbonate as previously described (10,13) to obtain MeCS and MeTriCS.

Methyl Dicarboxystearate (MeDiCS)

MeDiCS was extracted from either oxidized-hydroformylated safflower or soybean methyl esters with either

TABLE IV

Mechanical Properties of Polyvinyl Chloride (PVC) Sheets Containing 32% Plasticizer

No.	Stearate ester[a]		Torsional stiffness (C)		Compatibility (Δ)	Tensile strength (psi)	Elongation (%)	100% Modulus (psi)	Migration wt loss (%)	Volatility wt loss (%)	Heat sstability (hr)
	Terminal alkyl	Internal carboalkoxy	T_f	T_4							
					Hydroformylated samples						
1	Me	9(10)-Me	-47	-13	34	2440	290	915	18.7	4.1	b,c
2	Me	MeDi- 87%, tri 13%	-27	-3	24	2840	410	885	6.2	0.8	4.5^{b}
3	Me	MeDi- 81%, mono 12%, tri 7%	-33	-6	27	2670	310	905	9.1	1.3	4.5^{b}
4	*n*-Bu	9(10)-*n*-Bu	-57	6	63	2255	240	1225	20.4	4.6^{d}	6.5^{b}
5	*n*-Bu^{e}	*n*-Bu	-58	11	69	2380	310	1180	20.1	4.7^{d}	6.5^{b}
6	*n*-Bu	Di-*n*-Bu	-40	-6	34	2615	300	1070	10.8	1.0	6.5^{b}
7	*n*-Bu^{f}	Tri-*n*-Bu- 91%	-28	-1	27	2555	255	1170	5.4	0.6	5^{b}
8	Et	DiMe	-32	-7	25	2255	245	995	9.2	0.9	8^{g}
9	*i*-Pro	DiMe	-33	-5	26	2770	345	1010	7.8	0.9	8^{g}
10	*n*-Bu	DiMe	-33	-7	26	2745	345	920	8.2	0.6	7^{g}
11	EtHex	DiMe	-34	-1	33	2765	285	1255	8.0	0.7	7^{g}
12	Dmp	DiMe	-30	1	31	2890	295	1435	5.5	0.6	6.5^{g}
13	Me	DiEt	-35	-8	27	2810	360	1110	10.7	0.8	6.5^{g}
14	Et	DiEt	-37	-7	30	2780	345	1145	10.4	0.8	6.5^{g}
15	*n*-Bu	DiEt	-39	-6	33	2660	325	1130	10.9	0.8	6.5^{g}
16	EtHex	DiEt	-39	2	41	2905	335	1390	10.5	1.0	6.5^{g}
					Hydrocarboxylated samples						
17	Me	Me^{h,i}Di- 66%, Mono 28%, tri 5%	-32	-6	26	2700	370	875	8.4	1.8	2^{b}
18	Me	Me^{h}Di- 77%, mono 3%, tri 20%	-23	-1	22	2750	340	960	4.7	0.9	2^{b}
19	*n*-Bu^{f}	*n*-Bu^{h,i}Di- 58%, mono 42%	-43	-7	36	2465	250	1070	12.3	1.0	3.5^{b}
20	*n*-Bu^{f}	*n*-Bu^{h}Di- 97%	-37	-4	33	2575	340	1130	8.8	0.9	4^{b}
21	Me	Me^{j}Di- 49.4%, mono 1.2%, tri 49.4%	-20	2	22	2715	310	970	3.4	0.8	2^{b}
22	*n*-Bu^{f}	*n*-Bu^{i,j}Di- 42%, mono 37%, tri 20%	-36	-5	31	2635	320	1065	8.6	0.9	3.5^{b}
23	*n*-Bu^{f}	*n*-Bu^{j}Di- 46%, mono 13%, tri 41%	-31	-2	29	2575	315	1055	6.1	0.8	3.5^{b}
		Controls:^{k} DOP	-25	4	29	2835	290	1165	3.0	1.5	6.5^{b}
			-27	-2	29	2705	390	1275	4.1	1.2	8.0^{g}
		DOS	-57	-7	50	2355	295	1045	19.3	1.6	b,c
		Plastolein 9720	-21	8	29	2830	305	1345	3.9	0.9	7.5^{g}

[a] Me = methyl; Et = ethyl; *i*-Pro = isopropyl; *n*-Bu = *n*-butyl; EtHex = 2-ethylhexyl; Dmp = 2,2-dimethylphentyl.

[b] In % by wt: Geon 101 (commercial PVC resin), 65; plasticizer, 32; G 62 (epoxidized soybean oil stabilizer), 1; Mark M. (Ba-Cd complex), 2; milling as reported (21) gave3 x 6 x 0.075 sheets.

[c] Not determined.

[d] Exudate after 24 hr.

[e] From commercially available carboxystearic acid (Badische Anilin- und Soda-Fabrik, Wyandotte Corp., Parsippany, NJ).

[f] Mixture of methyl and butyl esters.

[g] Geon 102EP, 65; plasticizer 32; G 62, 2%; Vanstay RR (Ba-Cd complex), 1.

[h] From soybean methyl esters.

[i] Crude esters.

[j] From linseed methyl esters.

[k] DOP = di-2-ethylhexyl phthalate; DOS = di-2-ethylhexyl sebacate; Plastolein 9720 = commercial polymeric plasticizer.

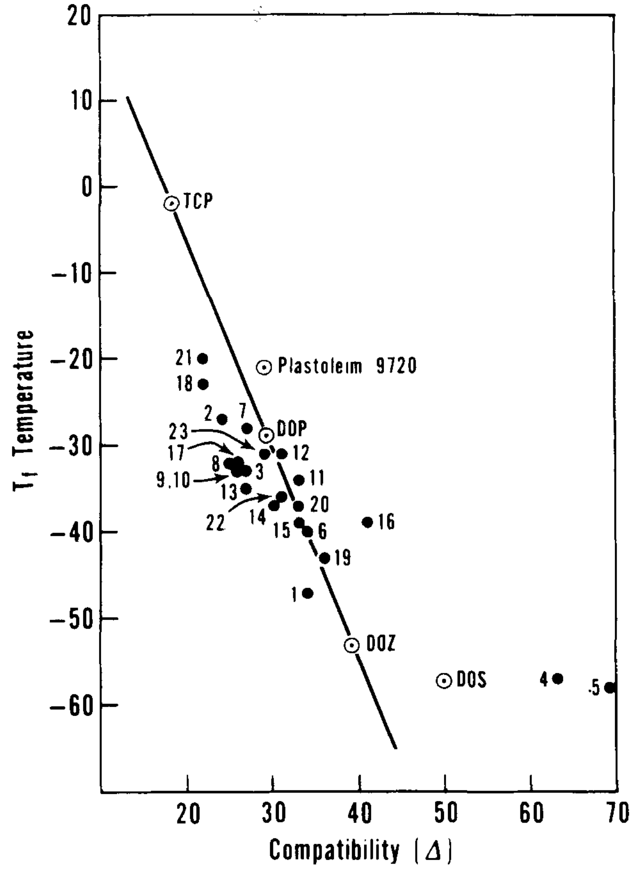

FIG. 1. Compatibility of experimental plasticizers with polyvinyl chloride compared to standard line (17). Numbers refer to samples given in Table IV. TCP = tricresylphosphate; DOZ = di-2-ethylhexyl azelate; DOS = bis(2-ethylhexyl) sebacate; plastolein 9720 = commercial polymer plasticizer.

potassium bicarbonate (10) or sodium hydroxide.

A. From safflower methyl esters: For the oxidation with gaseous oxygen, a 2-liter MagneDrive autoclave (Autoclave Engineers, Erie, PA) was charged with 996 g of hydroformylated safflower methyl esters (8), 400 ml of water, and 100 g of 5% calcium naphthenate in naphthenic acid (14). The autoclave was sealed, evacuated, purged with oxygen, and pressurized to 50 psi with oxygen. Cooling maintained the temperature between 35 and 40 C. Additional oxygen was added as needed. After the reaction had subsided and cooling no longer was needed, the temperature was raised to 60 C for 2 hr. The reaction product was allowed to stand overnight under pressure. A sample analyzed by GLC contained 69.4% MeDiCS, 17.2% MeCS, 3.1% methyl stearate, 7.8% methyl palmitate, and small amounts of short chain oxidation products.

The reaction product was transferred to a separatory funnel and 300 ml of ether was added. The water layer was removed and 100 ml of 10% sulfuric acid was added to precipitate the calcium salts. The ether layer was washed with water. Removing the water layer also removed suspended calcium sulfate. The ether layer was extracted with portions of 5% sodium hydroxide (Table II). Each alkali fraction was extracted with 2 x 100 ml of ether. All ether layers were combined before extraction with the next portion of 5% sodium hydroxide.

Acidification of each alkali fraction with hydrochloric acid followed by normal work-up gave the products listed in Table II. Fractions 1-3 were combined to give 553.4 g of methyl dicarboxystearate. The neutral equivalent was 203; calc 193.

B. From soybean methyl esters: Soybean methyl esters (822 g) were hydroformylated as previously described. For the oxidation with molecular oxygen, 360 ml of water was added. The product was cooled and maintained at 20-25 C during the oxidation. The general procedure in part A was followed, except calcium naphthenate was omitted. After oxidation was complete, heat and vacuum were applied to the autoclave to distill the water. There was obtained 992 g of product.

The product (480 g) was dissolved in 400 ml of hexane and extracted with sodium hydroxide as described in part A. A second portion of 480 g was similarly extracted with sodium or potassium bicarbonate. The reagents, yields, and analysis of starting materials and products are shown in Table I.

Alkyl Mono-, Di-, and Tricarboalkoxystearates

A. From hydroformylation: These alkyl esters were prepared by refluxing for 60 hr, 500 g of either MeCS, MeDiCSA, or MeTriCSA with the appropriate alcohol (1500 ml) containing 5 ml of concentrated sulfuric acid. In these reactions, the theoretical amount of water was removed by azeotropic distillation with benzene. After addition of aqueous potassium bicarbonate (15-20 g) and distillation of the alcohol, the product was dissolved in ether and washed with water. After removal of the ether in vacuo, the product was passed through 200 g of alumina and then fractionated by successive distillations through a falling film still (20).

B. From hydrocarboxylation: Hydrocarboxylated soybean and linseed methyl esters were prepared as previously reported (11,12). The carboxylic acids were purified either as the sodium salts to remove saturates and keto byproducts (16) or as the esters by fractional distillation. For esterification, the carboxylic acids were treated with *n*-butyl alcohol, H_2SO_4, and benzene, and the mixture was refluxed for 5 days with azeotropic removal of water. The products were fractionally distilled to obtain mixtures of methyl and butyl esters (Table IV, Nos. 19,20,22,23). Samples containing 58-97% dicarboalkoxystearate (Nos. 17-19) were obtained from soybean methyl esters, and samples containing 20-49% tricarboalkoxystearate (Nos. 21-23) were obtained from linseed methyl esters.

Alkyl Dicarbomethoxystearate and Alkyl Dicarboethoxystearate

A solution of sodium hydroxide (13.3 g), water (6 ml), and methanol (300 ml) (or ethanol depending on starting triester used) was added to either methyl dicarbomethoxystearate (138 g) or ethyl dicarboethoxystearate (153 g). The solution was refluxed for 2 hr, cooled, and extracted 3 times with 100 ml hexane. The alkaline solution was diluted with water and again extracted twice with ether. From the combined ether-hexane solutions, 36.8 g of MeDiMe triester was recovered. After the aqueous layer was acidified, the product was extracted with ether, washed with water, and stripped to dryness in vacuo. There was obtained 98 g (73.7% of theory) of dicarbomethoxystearic acid. Benzene (150 ml), the appropriate alcohol (200 ml), and concd. sulfuric acid (1 ml) were added to DiMeCA, and the solution was refluxed in a flask equipped with a Dean-Stark trap and condenser. When the theoretical amount of water was collected, the reaction was quenched by pouring the solution into aqueous sodium bicarbonate. In esterifications with lower alcohols where water could not be removed by azeotripic distillation, the reaction was carried out by following the acid value. A 1 ml sample of the CSA-alcohol mixture was titrated with standard alkali. Sulfuric acid catalyst was added and a 1 ml sample was again titrated with standard alkali. Titration of a 1 ml sample taken periodically during reflux, less the amount required for the sulfuric acid, indicated the amount of organic acid remaining to be esterified.

The reaction mixture after treatment with sodium bicarbonate was extracted with ether, and the solution was washed first with 200 ml of 0.5% sodium hydroxide and then with water until neutral. After ether was removed, the alkyl dicarbomethoxy- and dicarboethoxystearates were purified by successive distillations through a falling film still. The various triesters of DiCSA prepared are shown in Table III.

Butyl Dicarbomethoxystearate (Bu-DiMe Triester) and Methyl Dicarbobutoxystearate (Me-DiBu Triester)

Butyl formyl safflower esters (99 g) were oxidized with potassium permanganate and extracted with potassium bicarbonate (10) to give butyl dicarboxystearate (33 g) with a neutral equivalent of 227 (calcd neutral equivalent is 214). The butyl diacid ester was treated with phosphorus trichloride (20), and the resulting diacyl chloride, butyl *bis*(chlorocarbonyl)stearate, was added dropwise to a cold solution (0-5 C) of methanol containing pyridine (13).

Similarly, Me-DiBu triester was prepared from safflower methyl esters.

Plasticizer Evaluation

Procedures for plasticizer evaluation have been reported previously (17,21).

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