

Preparation, Characterization and Evaluation of Mono- and Diesters of Carboxystearic Acid¹

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Differences in the reactivity of the terminal and branched carboxyl groups of carboxystearic acid, prepared by carboxylation of oleic acid with carbon monoxide, have been utilized in preparing monoesters. Monoesters of both types have been prepared, those in which the ester group is terminal and those in which the ester group is a branched substituent on the chain. Diesters of carboxystearic acid have also been prepared.

Physical, chemical, and spectral characteristics of the products have been determined. In addition, the viscosity, viscosity index, pour point, and compatibility as plasticizers for PVC have also been studied.

All the monoesters studied are incompatible with PVC, but dimethyl, diethyl, and dipropyl carboxystearate, as well as carbomethoxyoctadecyl acetate (from oleyl alcohol), are efficient, low temperature plasticizers at the 35% level. Di-*n*-butyl carboxystearate also has an exceptionally high viscosity index (169) and a low pour point (-54°C .).

Each of the three types of esters described has a characteristic infrared absorption spectrum in the carbonyl region.

IN OUR WORK on the carboxylation of oleic acid and other unsaturated fatty acids and esters (1), it soon became apparent that the introduced branched carboxyl group is different in its reactivity from the terminal one. Esterification of the branched carboxyl is much slower than that of the terminal group, and special methods must be used to obtain complete esterification. It is equally difficult to hydrolyze an ester of the branched carboxyl by saponification.

This difference in reactivity of the branched and terminal carboxyl groups suggested a method of obtaining some interesting and potentially valuable monoesters. In our earlier work (1), we reported on the preparation, among others, of dimethyl and dibutyl esters of carboxystearic acid. We are now reporting the preparation of the diethyl, di-*n*-propyl, di-2-ethylhexyl and diisobutyl esters of carboxystearic acid and the half methyl, butyl and 2-ethylhexyl esters, in which the ester group is in either the terminal position or in the branched position. In addition, we have prepared an interesting new mixed diester, carbomethoxyoctadecyl acetate from carboxyoctadecanol. The physical and viscometrical properties, and evaluation of the mono- and diesters as plasticizers for commercial poly(vinyl chloride) are also reported.

Preparation of the half esters, in which the alkyl group is attached to the branched carboxyl, is accomplished by the reaction of a diester with the stoichiometric amount of alkali to saponify only one of the ester linkages. Inasmuch as the terminal ester group is the more labile of the two, it is hydrolyzed leaving the branched ester intact.

Half esters, in which the ester group is attached

to the terminal carbon, are prepared directly from the dicarboxylic acid, allowing only sufficient reaction time for the more reactive terminal carboxyl group to become esterified.

Experimental

Starting Materials: Oleic acid was a high quality commercial grade; 80–85% oleic acid, no *trans* isomers, 3.5% polyunsaturated acids and the remainder predominantly palmitic acid. Oleyl alcohol, 98–99%, was prepared by a described procedure (2).

Preparation of Carboxystearic Acid: Although a small scale preparation of carboxystearic acid has been described (1), a larger scale procedure is given here for comparison and, in this case, using a commercial grade of oleic acid. To 2422 g. (24 moles) of 97.2% sulfuric acid in a 12-l. three-neck flask was added simultaneously from separate dropping funnels 283 g. (1 mole) of oleic acid and 141 g. (3 moles) of 98–100% formic acid. (Too rapid addition is inadvisable because of uncontrollable foaming.) The temperature was maintained between 10 and 20°C. by external cooling. In replicate experiments from 80 to 110 min. were required for addition of the reactants. Stirring was continuous for a total reaction time of four hr., using a half-moon blade type stirrer. The product was poured into approximately 3 l. of a mixture of ice and water and extracted with ether. The ether solution was washed free of sulfuric acid and dried over sodium sulfate. Evaporation of the ether from the filtered solution yielded 317 g. of a syrup-like material with an iodine number of 8.0, acid number 298, and saponification number 299. This product was distilled from an alembic flask. The fractions distilling at 215–225°C. (1.5 mm.) (57%) having acid numbers of from 325 to 341 (342 theoretical) were used in preparation of the esters. The yield of carboxystearic acid was substantially increased by redistillation of fractions of lower acid number.

Preparation of Diesters of Carboxystearic Acid: The dimethyl ester of carboxystearic acid was prepared by the dimethyl sulfate method (1) or by reaction of the acid with diazomethane. The di-*n*-butyl, diisobutyl, diethyl, and di-*n*-propyl esters were prepared by the base-catalyzed alcoholysis method (1). The di-*n*-butyl ester was also prepared by a conventional method using toluene to remove water azeotropically. In the latter method the acid number of the product was reduced to 4 in 240 hr. Similarly, the di-2-ethylhexyl ester, with an acid number of 7, was obtained in 264 hr. of refluxing. Longer refluxing did not reduce the acid number further in either case. The dimethyl and dibutyl esters were distilled from an alembic flask and had the same properties as pre-

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TABLE I
Characteristics of Purified Products
Diesters of type $\text{CH}_3(\text{CH}_2)_x\text{—CH—}(\text{CH}_2)_y\text{COOR}$
 COOR ($x + y = 15$)

R	Boiling Point		n_{D}^{20}	d_{4}^{20}	Molecular Refraction		Carbon, %		Hydrogen, %	
	°C.	mm.			Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl ^a	146	0.35	1.4465
Ethyl.....	188	0.90	1.4458	0.9175	112.0	111.7	71.8	71.7	11.5	11.4
<i>n</i> -Propyl.....	200	0.80	1.4460	0.9123	121.3	120.6	72.8	72.8	11.7	11.7
<i>n</i> -Butyl ^a	180	0.40	1.4465
Isobutyl.....	200	0.15	1.4449	0.9007	130.6	130.2	73.6	73.7	11.9	11.9
2-Ethylhexyl.....	180	0.016	1.4522	0.8963	167.8	166.5	76.0	75.9	12.4	12.5
Carbomethoxyoctadecyl acetate ^b	140	0.07	1.4468	0.9220	107.4	107.4	71.3	71.5	11.4	11.7

Monoesters of type $\text{CH}_3(\text{CH}_2)_x\text{—CH—}(\text{CH}_2)_y\text{COOH}$
 COOR ($x + y = 15$)

Methyl.....	178	0.40	1.4531	0.9461	98.1	97.9	70.1	70.3	11.2	11.3
<i>n</i> -Butyl.....	186	0.28	1.4528	0.9328	112.0	111.4	71.8	71.3	11.5	11.5

Monoesters of type $\text{CH}_3(\text{CH}_2)_x\text{—CH—}(\text{CH}_2)_y\text{COOR}$
 OOH ($x + y = 15$)

Methyl.....	160	0.08	1.4545	0.9523	98.1	97.5	70.1	70.0	11.2	11.2
<i>n</i> -Butyl.....	206	0.07	1.4540	0.9381	112.0	111.0	71.8	71.1	11.5	11.4
2-Ethylhexyl ^c	180	0.015	1.4564	0.9265	130.6	129.4	73.6	73.1	11.9	11.9

^a Previously reported (Ref. 1).

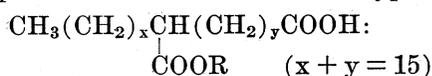
^b Note that this ester is different from those above. Its formula is $\text{CH}_3(\text{CH}_2)_x\text{—CH—}(\text{CH}_2)_y\text{CH}_2\text{C(=O)CH}_3$

^c Acid number 137 (calcd. 127).

viously described (1). A successful distillation of the dimethyl ester was also obtained using a heated 8-in. Vigreux column. The diethyl, dipropyl, and diisobutyl esters were all distilled readily through the Vigreux column.

The di-2-ethylhexyl ester of carboxystearic acid could be purified only by molecular distillation. From 104 g. of crude diester, 73 g. of substantially pure product was obtained from 170 to 190°C. at 16 μ : n_D^{20} 1.4523; acid no. 9. Analysis of the heart fraction is shown in Table I.

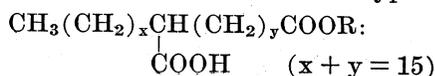
Preparation of monoesters of the type



An equimolar quantity of NaOH in a 50% aqueous alcoholic solution was added slowly with stirring and heating to an alcoholic solution of the diester (1.25 ml., 95% ethanol per g.). The temperature was allowed to rise to 70°C. After a few minutes of stirring at this temperature the mixture was cooled and acidified with dilute hydrochloric acid. The product was recovered by extraction with ether. The half methyl ester, prepared in this manner, had an acid number of 168 (calcd., 164). Similarly the half butyl ester had an acid number of 127 (calcd., 146). Distillation of these half esters from an alembic flask yielded substantially pure products.

When treated in a similar manner, the di-2-ethylhexyl ester of carboxystearic acid yielded a product having an acid number of only 44 (calcd., 127). Heating the reaction mixture at 70°C. for 1½ hr. increased the acid number to 101. The acid number remained unchanged even when heating was continued for 5 hr. at 100°C. No separation was obtained by molecular distillation of the product. This preparation was, therefore, abandoned.

Preparation of monoesters of the type



Half esters of this type were prepared by a method in which 5 ml. of the alcohol per g. of carboxystearic acid and 2% by weight of naphthalene 2-sulfonic acid, based on carboxystearic acid, were refluxed. The time of refluxing was sufficient to esterify only the more reactive terminal carboxyl group, and was determined by trial for each alcohol used. Starting in each case with 40 g. of carboxystearic acid (acid number 333–340) the time of refluxing with methanol was 40 min., with butanol 19 min., and with 2-ethyl-1 hexanol⁷ 7 min. The acid numbers of the crude half esters obtained in this manner were: methyl half ester 158 (calcd. 164), butyl half ester 149 (calcd. 146), and 2-ethylhexyl half ester 146 (calcd. 127). The half methyl and butyl esters were distilled from an alembic flask; the 2-ethylhexyl half ester was distilled in a molecular still from 170 to 180°C. at 15 μ .

Preparation of Carbomethoxyoctadecyl Acetate: To 74 g. (0.23 mole) of undistilled methyl ester of carboxyoctadecanol (1) was added 47 g. (0.46 mole) of acetic anhydride. The mixture was stirred for 2 hr. at 110°C. Hot water was added slowly, and stirring was continued for an additional 10 min. to hydrolyze excess acetic anhydride. The product was extracted with ether and washed with water to remove acetic acid. Small amounts of ethanol were used to aid in breaking troublesome emulsions. Evaporation of the dried ether solution yielded 77 g. of a dark brown mobile liquid with an acid number of 8.8 and saponification number 141. This product was distilled from an alembic flask. From 75 g., 40 g. of a colorless substantially pure product was obtained, b.p. 135–140°C. (0.07 mm.), acid number 7, and saponification number 155. Analysis of the heart fraction gave a saponification number of 151 (calcd. for one functional group, 151). Other data are shown in Table I.

Infrared Spectra: Infrared absorption spectra were obtained on a Perkin Elmer Model 21 double beam recording spectrophotometer. For general spectra, a demountable cell consisting of sodium chloride windows (one window with a moat-type channel) (3), and 0.025 and 0.03 mm. spacers were used since all samples were liquid.

Viscometrical and Plasticizing Properties of Esters of Carboxystearic Acid and Carbomethoxyoctadecyl Acetate:

Starting Materials: The esters used as plasticizers were prepared as described above. They were of high purity but were taken over a broader distillation range than the heart fractions used for ultimate analyses shown in Table I. The acid number of these esters, shown in Table II, gives an indication of the degree of purity. Commercial poly(vinyl chloride) (Geon 101) was used for the plasticizer studies. Vinyl stocks were stabilized with a Ba-Cd complex (Mark M.). The standard recipe was as follows: Geon 101 65%, plasticizer 34%, and stabilizer 1%. Commercial plasticizers used for controls were di-2-ethylhexyl phthalate (DOP) and di-2-ethylhexyl sebacate (DOS).

Test Methods: The preparation of the poly(vinyl chloride) compositions and the determination of tensile strength, 100% modulus, elongation, torsional modulus, volatility, light stability and compatibility of plasticizers were obtained by previously reported methods (4,5,6).

Results and Discussion

Preparation (Table I): The method chosen for the preparation of diesters of carboxystearic acid is a matter of expedience. Several factors enter in this choice. For example, in preparing the normal dibutyl ester, three methods were employed. In a conventional acid-catalyzed method using toluene as an entraining agent for removal of water, approximately ten days of refluxing is required to obtain nearly complete esterification. By the use of cymene to elevate the boiling point of the refluxing mixture, the time required to esterify carboxystearic acid is reduced, but difficulty is experienced in removal of the cymene due to foaming during vacuum distillation. This was the least satisfactory of three methods used. In the base-catalyzed alcoholysis method, using the dimethyl ester, the time is the shortest of all, approximately 24 hr. In this method, however, care is required to determine if the exchange is complete. Also one must take into consideration the time required in preparing the dimethyl ester.

The fact that the branched carboxyl group of carboxystearic acid is difficult to esterify, and once esterified, equally difficult to saponify, facilitates the preparation of the half esters. Half esters, in which the ester group is in the branched position are prepared from the diester by addition of the stoichiometric amount of sodium hydroxide to saponify the more labile terminal ester. This takes place readily with the half methyl ester. In preparing the half-butyl ester the rate is somewhat slower and in the preparation of the 2-ethylhexyl half ester saponification of the terminal ester is incomplete. Unfortunately the di-2-ethylhexyl ester is not separated from the half 2-ethylhexyl ester by molecular distillation.

Half esters in which the ester group is in the terminal position are readily prepared by refluxing carboxystearic acid with the appropriate alcohol for a length of time sufficient to react only with the more reactive terminal carboxyl group. Table I lists the properties of the monoesters prepared.

Each of the three types of esters described has a characteristic infrared absorption spectrum in the carbonyl region. A typical example is shown in Figure 1 for the mono- and di-*n*-butyl esters of carboxystearic acid. No splitting of the carbonyl band is observed in the diesters. The two types of monoesters are readily distinguishable by absorption in the carbonyl region. If the ester group is in the side chain, the frequency difference between the ester carbonyl band and the acid carbonyl band is 15 to 20 cm.⁻¹; if the ester group is terminal, this difference is 35 to 40 cm.⁻¹

Viscometrical Characteristics (Table II): The viscosity index increases with increase in chain length of alkyl group in the diesters of carboxystearic acid, ranging from a minimum of 97 with the dimethyl ester to a maximum of 169 with the di-*n*-butyl ester. The viscosity index of the latter is superior to that of di-2-ethylhexyl sebacate.

The pour point decreases in the same order but the minimum pour point of -54°C. obtained with the dibutyl ester is not as low as that of di-2-ethylhexyl

TABLE II
Viscometrical Characteristics of Mono- and Diesters
Diesters of type CH₃(CH₂)_x-CH-(CH₂)_yCOOR
COOR (x + y = 15)

R	Acid number	Kinematic Viscosity in Centistokes at °C.							A.S.T.M. slope	V.I.	Pour point, °C.
		98.8	38.0	10	-10	-20	-30	-40			
Methyl.....	3.6	2.96	12.5	41.9	146	0.75	97	-25 ^a
Ethyl.....	3.7	3.05	12.6	37.9	125	313	959	2,700 ^b	0.75	112	-44
<i>n</i> -Propyl.....	5.1	3.50	14.3	45.4	151	337	841	2,800 ^b	0.71	133	-45
<i>n</i> -Butyl.....	5.9	3.85	15.3	51.0	162	297	721 ^b	0.70	169	-54
Isobutyl.....	2.5	3.88	17.5	61.5	246	560	1,594	4,555	0.73	135	-52
2-Ethylhexyl.....	4.8	5.88	32.3	128	555	1,170	3,440	11,760	0.69	134	-45
Carbomethoxyoctadecyl acetate ^d	6.7	3.74	18.4	70.4	290	608 ^b	0.76	100	-47
Monoesters of type CH ₃ (CH ₂) _x -CH-(CH ₂) _y COOH COOH (x + y = 15)											
Methyl.....	167	10.5	94.7	555	3,400 ^b to 4,100	0.67	102	-22
<i>n</i> -Butyl.....	140	10.7	83.7	412	1,930	4,930	16,940	0.63	118	-36
Monoesters of type CH ₃ (CH ₂) _x -CH-(CH ₂) _y COOR COOR (x + y = 15)											
Methyl.....	166	10.3	90.3	469	2,390	6,400 ^b	0.70	104	-48 ^a
<i>n</i> -Butyl.....	160	13.1	115	651	3,370	7,780	27,490	0.63	114	-35
2-Ethylhexyl.....	144	16.8	183	1,120	7,090	17,760 ^c	0.65	104	-42
Control bis(2-ethylhexyl sebacate) (DOS).....	3.62	12.6	37.2	118	238	550	1,338	0.71	145	-67

^a Freezing point; the material was a solid white crystalline mass.

^b Sample began to crystallize; readings were erratic.

^c Viscosity too high to measure at -30°C.

^d Note that this ester is different from those above. Its formula is CH₃(CH₂)_x-CH-(CH₂)_yCH₂COOCH₃

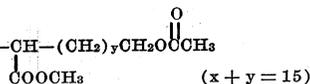


TABLE III
Comparison of Properties of Commercial Poly(Vinyl Chloride) (Geon 101)
Plasticized with Diesters and Commercial Plasticizers

$\begin{array}{c} \text{Diesters of type} \\ \text{CH}_3(\text{CH}_2)_x-\text{CH}-(\text{CH}_2)_y\text{COOR} \\ \text{COOR} \quad (x+y=15) \\ \text{R}^a \end{array}$	Tensile strength, p.s.i.	Elongation, %	Modulus, 100%, p.s.i.	Clash-Berg		Migration, % wt. loss after 14 days	Volatility wt. loss, %
				$T_{135,000}$, °C.	$T_{10,000}$, °C.		
Methyl.....	2500	340	1200	-41	-8	13	6.6
Ethyl.....	2600	310	1100	-48	-6	16	5.6
<i>n</i> -Propyl.....	2400	310	1100	-50	-6	16	2.7
<i>n</i> -Butyl.....	1900	220	1200	-57	+2	17	5.0
Isobutyl.....	2500	330	1300	-47	+9	16	6.7
Carbomethoxyoctadecyl acetate ^b	2400	310	1000	-47	-6	16	3.8
Controls							
Di-2-ethylhexyl phthalate (DOP).....	2600	330	1100	-30	0	4	1.6
Di-2-ethylhexyl sebacate (DOS).....	2950	370	1400	-59	-19	23	2.0

^a The same samples used for viscosity characteristics (Table II) were used here.

^b Note that this ester is different from those above. Its formula is $\text{CH}_3(\text{CH}_2)_x-\text{CH}-(\text{CH}_2)_y\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_3$
 COOCH_3 (x + y = 15)

sebacate. The pour points of all the dialkyl esters of carboxystearic acid are fairly low, with the exception of the dimethyl ester. Carbomethoxyoctadecyl acetate has a low pour point, also (-47°C.).

Noteworthy are the pour points of the monoesters, methyl carboxystearate (-48°C.) and 2-ethylhexyl carboxystearate (-42°C.). Even though these compounds have a free carboxyl group, their pour points are low, probably because they are a mixture of position isomers.

Plasticizer Evaluation (Table III): All the half esters are incompatible with poly(vinyl chloride), with no fusion on milling. This result was anticipated as compounds with free carboxyl groups are notoriously incompatible with PVC.

Certain diesters, however, are compatible with poly(vinyl chloride) at the 35% level. These are the dimethyl, diethyl, and di-*n*-propyl esters of carboxystearic acid and carbomethoxyoctadecyl acetate. These diesters are efficient plasticizers, as shown by the relatively low modulus figures, and they are efficient at low temperatures. The Clash-Berg $T_{135,000}$ values range from -41°C. (dimethyl ester) to -57°C. (di-*n*-butyl ester). Comparison of the $T_{10,000}$ with the $T_{135,000}$ figures indicates a relatively slow increase in modulus with decrease in temperature, a desirable characteristic. The modulus-temperature curves for these diesters are not as shallow as that of di-2-ethylhexyl sebacate.

The dibutyl and diisobutyl esters of carboxystearic acid, at the 35% level in PVC, showed a heavy exudate after 24 hr. Di-2-ethylhexyl carboxystearate and PVC did not even fuse on milling. This is in line with previous results which show a ratio of twelve carbon atoms to one ester linkage is about the maximum for compatibility. In the last case, there is a ratio of 35 to 2.

The migration weight losses for the diesters are slightly lower than that of DOS but higher than that of DOP. Volatility losses are higher in the new diesters than in the controls.

In the heat stability test in air at 160°C., the PVC specimens containing the diesters turned black in 2½ to 3 hr., as did the controls containing DOP.

In the light stability test, samples containing dimethyl and dipropyl esters of carboxystearic acid were equal to the controls with DOP, which showed little or no change to 216 hr. when the test was discontinued. The samples containing the diethyl ester of carboxystearic acid and those containing carbo-

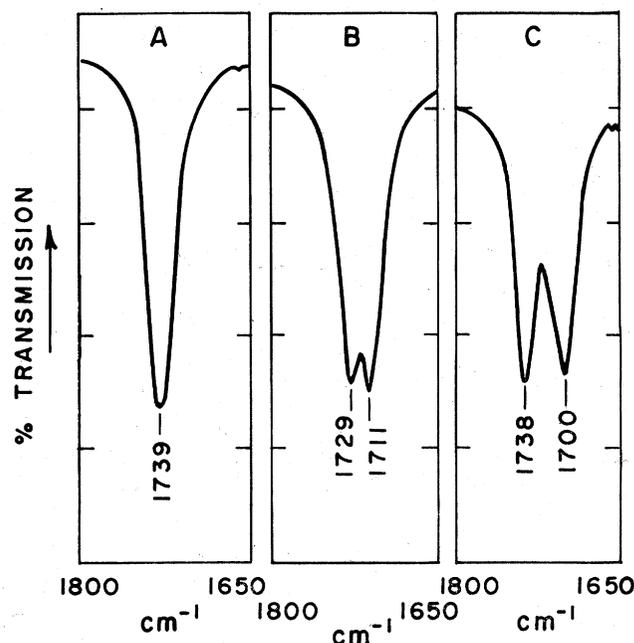


Fig. 1. Section of infrared spectra of *n*-butyl esters of carboxystearic acid.

- A. Diester.
B. Monoester, ester in branched position.
C. Monoester, ester in terminal position.

methoxyoctadecyl acetate showed increased spotting after 144 hr.

No attempts were made to prepare compositions of maximum attainable heat and light stability.

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