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

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ABSTRACT

Conditions were determined for selective alkaline transesterification of methyl 9(10)-carbomethoxystearate. With 2,2-dimethylpentanol and 2-ethylhexanol, the corresponding alkyl 9(10)-carbomethoxystearates were obtained in good yield. These two mixed alkyl diesters, along with other alkyl esters of mono-9(10)-, di- and tricarboxystearic acids prepared by conventional methods, were evaluated as lubricants. Several esters compared favorably with dioctyl sebacate used as the control. The esters had high viscosity indices and low American Society for Testing and Materials slopes. The pour point of purified dimethylpentyl 9(10)-carbomethoxystearate is below -70 C. Several esters have antiwear properties when added to the control oil.

INTRODUCTION

Each year industrial and military specifications for lubricants become more stringent. Military specifications (Mil-L-23699) for aircraft turbine engine lubrication require an oil with a viscosity of 5.0-5.5 centistokes at 210 F and at least 25.0 centistokes at 100 F, a maximum pour point of -65 F and a minimum flash point of 425 F (1). Certainly, future lubricating oils with oxidative stability and corrosion resistance for operation considerably above 500 F (possibly as high as 1000 F) will be needed (2). Various classes of compounds, such as esters, ethers, fluorocarbons, silicones, and others, have been evaluated as possible lubricants and additives (3-8).

Generally, esters have been favored over other compound classes because of their superior lubricity coupled with good temperature stability, fluidity at low temperature and excellent resistance to corrosion and oxidation. At present, esters of dibasic acids, such as di-2-ethylhexyl sebacate (DOS), barely meet certain military requirements even with special compounding, including the addition of efficient antioxidants. Possible substitutes for DOS have now been prepared by esterifications of methyl 9(10)-mono-, di-, and tricarboxystearates (MeCS, MeDiCS, and MeTriCS). These acidic methyl esters are prepared by selective hydroformylation (9) and oxidation (10) processes carried out on unsaturated fatty esters derived from oils containing oleate, linoleate, and linolenate. This article reports the preparation and evaluation of some of these new esters.

RESULTS

For simplicity, the complex esters derived from carboxystearic acid (CSA) and from MeCS will be abbreviated. The terminal alkyl ester will be named first, followed by the branched ester group; for example, butyl 9(10)-carbomethoxystearate becomes Bu-Me diester.

Diesters

Various dialkyl esters of CSA used for the lubricant evaluation studies were prepared by direct acid catalyzed esterification-transesterification procedures determined in a kinetic study (10).

Alkyl esters of CSA containing two different alkyl groups, however, are more difficult to prepare by direct esterification procedures. The terminal carboxyl group in 9(10)-CSA is ca. 26-27 times more reactive than the branched carboxyl group (10). Because of this difference in reactivity, Roe, et al., (11) was able to carry out a selective saponification of the labile terminal ester moiety to obtain various carboalkoxystearic acids. However, their CSA products were derived from the Koch reaction on oleic acid and possibly may contain methyl branching at the internal carboxyl functionality (9,12); therefore, their products should not be considered identifical to those from a rhodium catalyzed hydroformylation process.

This difference in reactivity also permitted the selective alkaline transesterification of the terminal ester of Me-Me diester with 2,2-dimethylpentanol (Dmp-OH) and 2-ethylhexanol (EtHex-OH) to yield the desired Dmp-Me and EtHex-Me diesters (Table I). Conversions to Dmp-Me (98.5%) and EtHex-Me (97%) diesters were highest when enough anhydrous alcohol, containing 12 mg dissolved sodium, was added to make a 0.28 molar (10 wt %) solution of Me-Me diester. Under these conditions, reaction times to reach conversion above 97% differed sharply. With

TABLE I

Transesterification of Methyl 9(10)-Carbomethoxystearate

Me-Me moles	Sodium, mg	Vol, ml	Time	Diester[a]		
				Me-Me	R-Me	R-R
2,2-Dimethylpentanol				R = Dimethylpentyl		
0.14	50	100	5 min	1.7	95.0	3.6
			5 hr	-	73.6	26.3
			24 hr	-	63.4	36.3
0.28	50	50	5 min	trace	43.6	56.3
			5 hr	-	25.8	74.2
			24 hr	-	7.3	92.2
0.28	25	50	5 min	trace	93.4	6.5
			5 hr	-	92.1	7.9
			24 hr	-	69.0	31.0
0.28	12	50	5 min	21.4	78.6	trace
			5 hr	2.2	97.2	0.5
			24 hr	0.8	98.5	0.8
0.56	12	25	5 min	55.9	44.1	-
			5 hr	31.7	68.3	-
			24 hr	26.3	73.7	-
2,Ethylhexanol				R = Ethylhexyl		
0.14	50	100	5 min	-	43.5	56.5
			5 hr	-	41.9	58.1
			24 hr	-	27.6	72.3
			72 hr	-	7.0	92.9
0.28	50	50	5 min	-	2.0	98.0
			5 hr	-	trace	99.0
0.28	25	50	5 min	-	89.5	10.5
			5 hr	-	81.8	18.2
			24 hr	-	65.0	34.9
			72 hr	-	43.2	56.8
0.28	12	50	5 min	-	97.0	2.9
			5 hr	-	94.4	5.5
			24 hr	-	90.9	9.0
0.56	12	25	5 hr	5.5	89.2	5.2
			24 hr	5.4	88.7	5.8

[a] Percentage by gas liquid chromatographic analysis.

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[1] ARS, USDA.

TABLE II

Viscosity Characteristics[a] of Di-, Tri-, and Tetraesters of Carboxystearic Acid

Stearates		Before oxidation				After oxidation			
Alkyl	Carboalkoxy	Kinematic viscosity Cs[b] at F		Viscosity index	ASTM slope	Kinematic viscosity Cs at F		Viscosity index	ASTM slope
		100	210			100	210		
Methyl	Methyl	11.1	2.8	106	0.76	17.9	3.8	115	0.75
Methyl	Dimethylpentyl	16.3	3.6	114	0.74	21.5	4.3	116	0.74
Methyl	Ethylhexyl	15.8	3.7	129	0.72	19.8	4.1	121	0.72
Dimethylpentyl	Methyl[c]	21.2	4.3	120	0.72	30.0	5.4	127	0.71
Dimethylpentyl	Methyl[d]	21.3	4.4	125	0.72	26.8	4.9	116	0.73
Ethylhexyl	Methyl	19.3	4.2	138	0.71	7.9	1.6		0.98[e]
Butyl	Butyl	13.5	3.5	155	0.69	15.9	3.8	142	0.71
Dimethylpentyl	Dimethylpentyl	30.1	5.4	126	0.70	40.9	6.5	121	0.76
Ethylhexyl	Ethylhexyl	25.3	5.1	150	0.67	31.2	5.8	140	0.67
Butyl	Dibutyl	24.2	4.9	141	0.70	30.4	5.6	137	0.70
Butyl	Tributyl	37.5	6.5	136	0.68	51.7	7.5	119	0.70
Controls									
Dioctyl sebacate		13.2	3.4	154	0.69	12.5	3.3	158	0.69
Paraffin oil (102)		21.9	3.9	63	0.79	24.9	4.2	70	0.80

[a] American Society for Testing and Materials (ASTM) D445-65 and ASTM D341-43.

[b] Cs = centistokes.

[c] Acid value 0.

[d] Acid value 2.1.

[e] Estimated.

Dmp-OH, equilibrium was reached in 24 hr, whereas EtHex-OH reached maximum conversion in 5 min. The extreme difference in transesterification time between Dmp-OH and EtHex-OH is attributed to steric hindrance in Dmp-OH (10). With EtHex-OH, reaction times longer than 5 min shifted equilibrium to yield EtHex-EtHex diester. Increasing the amount of dissolved sodium catalyst from 12 to 50 mg/50 ml reaction mixture gave 99% conversion to EtHex-EtHex diester. In reactions where conversion to the desired mixed diester was low because of insufficient catalyst, small amounts of sodium alkoxide were added to shift equilibrium to the mixed diester. Larger amounts of catalyst resulted in complete transesterification.

Although it may be possible to prepare the other possible isomeric esters (Me-Dmp and Me-EtHex diesters) by transesterification of Dmp-Dmp and EtHex-EtHex diesters with methanol, these mixed esters were prepared directly by addition of the acid chloride of MeCS to the appropriate alcohol (10).

Tri- and Tetraesters

Frankel and Thomas (13) hydroformylated methyl esters of polyunsaturated oils to obtain methyl stearates having more than one formyl group. Thus, safflower and linseed methyl esters containing linoleate and linolenate, when hydroformylated and oxidized with permanganate, yielded MeDiCS and MeTriCS, respectively.

When compared with methyl stearate containing one branched carboxyl group, methyl stearates with two more branched carboxyl groups are much more acidic and can be treated as straight chain aliphatic acids. Advantage was taken of this property to separate MeDiCS from MeCS. MeDiCS was obtained almost quantitatively and in 95% purity by extraction of a mixture containing MeCS and MeDiCS with aqueous sodium bicarbonate. MeCS and any remaining MeDiCS in the organic phase then were removed from nonacidic by-products (14) (methyl stearate, methyl keto-, and hydroxystearate) by extraction with sodium hydroxide. In a similar manner, extraction of oxidized-hydroformylated linseed methyl esters with small amounts of aqueous methanolic sodium bicarbonate gave 91.5% pure MeTriCS. Subsequent aqueous bicarbonate extractions yielded mixtures with varying amounts of MeDiCS and MeTriCS.

Acid catalyzed transesterification and esterification of MeDiCS and MeTriCS with 1-butanol (Bu-OH) gave the desired butyl di- and tricarbobutoxystearates (Bu-DiBu triester and Bu-TriBu tetraester.

Lubricant Evaluation

Viscosity characteristics of various carboxystearate esters are shown in Table II. Viscosity index and American Society for Testing and Materials (ASTM) slope measure change in viscosity with temperature, i.e. the higher the viscosity index and lower the slope, the smaller the change in viscosity with change in temperature. Viscosity indices of the esters studied compared favorably with DOS and greatly exceeded the viscosity index of the 102 paraffin oil control. The kinematic viscosities at various temperatures for the Bu-Bu diester were almost identical to DOS control. As shown in Table II, oxidation had some effect upon viscosity and ASTM slopes of the various esters evaluated. Only the Dmp-Dmp and EtHex-EtHex diesters met with Mil-L-23699 specifications for viscosity at 100 and 210 F.

Table III lists the antiwear data for the samples tested as base oils and as additives in DOS and Topaz S105 oil (similar to 102 paraffin oil). Extreme pressure data also are listed for the ester samples tested as base oils. Although the various esters tested have only ordinary antiwear and extreme pressure weldpoints, the Bu-Bu, Dmp-Me diesters, Bu-DiBu triester, and Bu-TriBu tetraester possess antiwear additive properties at the 5% level in Topaz S105 oil. Wear scar data (Table III) for two samples of Dmp-Me diester, when evaluated as base oils, vary sharply. The Dmp-Me diester, which gave a good wear scar test of 0.632 mm, was redistilled fractionally and passed through alumina to remove residual acid present before testing (Table IV). The untreated product had a wear scar of 0.740. Thus, unknown acidic impurities, which were removed, probably had an adverse effect upon lubricity. Removal of impurities also may account for the absence of a cloud point and for the extremely low freezing point of below -70 C, which exceeded the -65 C for DOS and Mil-L-23699 specifica-

TABLE III

Antiwear, Extreme Pressure, Cloud, Pour, and Freezing Points of Di-, Tri- and Tetraesters of Carboxystearic Acid

Stearates							
Alkyl	Carboalkoxy	Base oil	Average wear[a] scar, mm	Extreme pressure weld point,[b] kg	Cloud point,[c] C	Pour point,[c] C	Freezing point,[c] C
Methyl	Methyl	100% Stearate	0.882	120	+1	-35	-38
Methyl	Dimethylpentyl	100% Stearate	0.823	130	None	-58	-61
Dimethylpentyl	Methyl[d]	100% Stearate	0.632	110	None	<-70	<-70[e]
Dimethylpentyl	Dimethylpentyl	100% Stearate	0.720	120	-48	-48	-51
Butyl	Butyl	100% Stearate	0.912	120	-52	-56	-58
5% Butyl	Butyl	95% DOS[f]	0.942				
5% Butyl	Butyl	95% Topaz S105	0.622				
Dimethylpentyl	Methyl[g]	100% Stearate	0.740	100	-41	-51	-54
5% Dimethylpentyl	Methyl	95% DOS	0.822				
5% Dimethylpentyl	Methyl	95% Topaz S105	0.635				
Methyl	Ethylhexyl	100% Stearate	0.798	110	-55	-59	-62
5% Methyl	Ethylhexyl	95% DOS	0.915				
5% Methyl	Ethylhexyl	95% Topaz S105	0.697				
Ethylhexyl	Methyl	100% Stearate	0.758	100	-38	-45	-48
5% Ethylhexyl	Methyl	95% DOS	0.855				
5% Ethylhexyl	Methyl	95% Topaz S105	0.832				
Ethylhexyl	Ethylhexyl	100% Stearate	0.980	110	-62	-53	-56
5% Ethylhexyl	Ethylhexyl	95% DOS	0.860				
5% Ethylhexyl	Ethylhexyl	95% Topaz S105	0.763				
Butyl	Dibutyl	100% Stearate	0.785	100	-45	-52	-55
5% Butyl	Dibutyl	95% DOS	0.918				
5% Butyl	Dibutyl	95% Topaz S105	0.620				
Butyl	Tributyl	100% Stearate	0.775	100	-18	-50	-53
5% Butyl	Tributyl	95% DOS	0.908				
5% Butyl	Tributyl	95% Topaz S105	0.650				
		Topaz S105 control	0.794	120			
		DOS control	0.872	120	-	-62	-65
		102 Paraffin oil control	0.803	100	-	0	- 2

[a] American Society for Testing and Materials (ASTM) D2266-67.

[b] ASTM D2596-67+.

[c] ASTM D97-66.

[d] Acid value 0.

[e] Sample flowed at limit of cooling bath (dry ice and alcohol).

[f] DOS = di-2-ethylhexyl sebacate.

[g] Acid value 2.1.

tions.

The pour points of 9(10)-carboxystearate esters reported in Table III are up to 10 C lower than the corresponding isomeric carboxystearates reported by Roe, et al. (11). Generally, pour points and freezing points ranged from -50 to -62 C and were somewhat higher than the DOS control.

Esters with acid values of zero before oxidation had values after oxidation for 19-34 as compared to values of 3-6 for esters containing 2% phenothiazine. Oxidized samples without inhibitor were dark brown to tarry black oils or emulsions containing varying amounts of sludge, whereas samples containing phenothiazine remained reddish amber throughout the test and contained little, if any, sludge. The reddish-amber color was caused by addition of phenothiazine.

Oxidation tests of di-, tri-, and tetraesters of CSA appear in Table IV. Since the acid values after oxidation were relatively high, these samples, apparently, are not stable under the test conditions. Fortunately, oxidative decomposition does not limit the use of these stearate esters as base oils, since phenothiazine, an excellent oxidation inhibitor, can be used to increase the stability of the base oil (Table IV).

In the absence of phenothiazine, a relatively high wt loss of 3-7% resulted during oxidation for some copper and steel test pieces. The wt loss of metal pieces in esters containing phenothiazine was low and comparable to the controls. Only the steel test piece in Bu-Bu diester with a 0.76% wt loss was above normal. Although some test pieces experienced a relatively high wt loss, they were only lightly tarnished or corroded. These appeared to have lost wt by reaction(s) other than oxidation.

EXPERIMENTAL PROCEDURES

Samples (ca. 1 mg) were treated with diazomethane and analyzed by gas liquid chromatography (GLC) programed from 180-300 C at 4 deg/min, 30 cc/min on an F & M model 5750 instrument equipped with a 6 ft x 1/4 in, 3% JXR column. Bu-OH, Dmp-OH, and EtHex-OH obtained from Eastman Kodak, Rochester, N.Y., were distilled before use. MeCS was prepared as previously described (10). Me-Dmp and Me-EtHex diesters were prepared by adding the acyl chloride of MeCS to the appropriate alcohol containing an equimolar amount of pyridine (10).

2,2-Dimethylpentyl 9(10)-Carbomethoxystearate (Dmp-Me Diester)

In a preliminary study of base catalyzed transesterification, a stock solution of sodium dimethylpentoxide was prepared by dissolving metallic sodium in Dmp-OH (50-55 mg Na/90 ml). A volume of stock solution containing the desired amount of dissolved sodium was diluted with Dmp-OH to 20, 45, or 95 ml and added to Me-Me diester (5 g) in a flame dried flask equipped with a magnetic stirrer, Drierite tube and septum. Samples for GLC analysis were withdrawn and immediately injected into the chromatograph for analysis (Table I).

For large scale preparation, a solution of sodium dimethylpentoxide in Dmp-OH, prepared from metallic sodium (340 mg) and Dmp-OH (1395 ml), was added rapidly to Me-9(10)-Me diester (155 g). The mixture was stirred for 2 hr at room temperature under anhydrous conditions. GLC analysis indicated 22% unreacted Me-Me diester. An

TABLE IV

Oxidation Tests on Di-, Tri-, and Tetraesters of Carboxystearic Acid[a]

Stearates		Visual appearance[b] after oxidation	Acid value		Percentage wt. loss of catalyst	
Alkyl	Carboalkoxy		Before oxidation	After oxidation	Copper	Steel
Without phenothiazine antioxidant						
Methyl	Methyl	Tarry black[c]	0.0	34.68	1.64[d]	0.51[d]
Methyl	Dimethylpentyl	Brown emulsion[e]	0.0	19.02	0.86[f]	4.07[f]
Dimethylpentyl	Methyl[g]	Tarry black[c]	0.0	28.67	1.40[f]	7.33[f]
Dimethylpentyl	Dimethylpentyl	Dark brown[e]	0.0	22.25	0.95[f]	3.91[f]
Purified dioctyl sebacate		Clear[h]	0.0	0.0	0.008[f]	1.13[f]
Paraffin oil (102)		Dark brown[e]	1.92	2.61	0.13[f]	1.01[f]
With 2% phenothiazine antioxidant[b]						
Butyl	Butyl		0.0	4.0	0.011[f]	0.760[d]
Dimethylpentyl	Methyl[i]		2.10	5.11	0.100[j]	0.003[k]
Methyl	Ethylhexyl		3.96	3.98	0.001[f]	0.065[f]
Ethylhexyl	Methyl		1.00	3.25	0.070[j]	0.100[f]
Ethylhexyl	Ethylhexyl		2.23	6.28	0.230[d]	0.0[k]
Butyl	Dibutyl		1.93	4.12	0.120[j]	0.040[f]
Butyl	Tributyl		0.0	3.69	0.100[j]	0.200[f]

[a] Modified American Society for Testing and Materials (ASTM) D943-54.

[b] All samples were water-white before oxidation. With phenothiazine samples were reddish-amber throughout tests.

[c] Heavy sludge.

[d] Medium tarnish and corrosion.

[e] Medium sludge.

[f] Light tarnish and corrosion.

[g] Redistilled; passed through alumina.

[h] Light sludge.

[i] One distillation.

[j] Heavy tarnish and corrosion.

[k] Clean or very light tarnish.

additional 100 ml Dmp-OH containing sodium (50 mg) was added and the solution stirred overnight. GLC analysis showed 96% conversion to Dmp-Me diester.

Glacial acetic acid (5 ml) was added and the excess acid neutralized with aqueous sodium bicarbonate. After the total volume was reduced to ca. 300 ml by distillation in vacuum, the product was dissolved in ether and washed with water. After distillation of the ether, water, and remaining Dmp-OH, the product was distilled in vacuum. The yield of Dmp-9(10)-Me diester was 147.5 g (74.5% of theory; 99% pure by GLC), boiling point 179-183 at 0.05 mm. Analysis: Calc. for $C_{27}H_{52}O_4$: C, 73.58; H, 11.89. Found: C, 74.00; H, 12.45.

2-Ethylhexyl 9(10)-Carbomethoxystearate (EtHex-Me diester)

After a preliminary study (Table I), sodium ethylhexoxide prepared from 350 mg sodium in anhydrous EtHex-OH (1050 ml) was added to Me-9(10)-Me diester (200 g). The reaction was quenched after 30 min with glacial acetic acid and the product isolated as described for Dmp-Me diester. The yield of EtHex-9(10)-Me diester was 211.3 g (82.2% of theory; 99^+% pure by GLC), boiling point 198-200 C at 0.07 mm. Analysis: Calc. for $C_{28}H_{54}O_4$: C, 73.95; H, 11.97. Found: C, 74.14; H, 12.40.

Methyl Dicarboxystearate (MeDiCS)

The product (397 g), obtained by hydroformylation of safflower methyl esters (13), was added to acetone (1000 ml) and water (500 ml) and then oxidized by slowly adding solid potassium permanganate (183 g). After decolorization in the usual manner by acidification with hydrochloric acid and addition of sodium bisulfite, the crude oxidized product was dissolved in ether and washed with water. The ether solution was cooled and extracted 5 times with 250 ml of 10% aqueous potassium bicarbonate. The combined potassium bicarbonate solutions were washed twice with ether and the ether layers combined. The ether solution contained MeCS and neutral products.

Ether was added to the aqueous potassium bicarbonate solution, and the mixture was acidified with hydrochloric acid. The ether layer then was washed with water and stripped to dryness. The yield of MeDiCS was 250.0 g, neutral equivalent, 200.9; calc. 193.7. GLC Analysis: 95.1% MeDiCS, and 4.9% MeCS.

The ether layer containing MeCS and neutral products was titrated with cold 50% sodium hydroxide to pH 10. The layers were separated. The ether layer then was titrated to a pH of 11 and separated. The process was repeated again to a pH of 12. The combined hydroxide solutions were extracted twice with ether and acidified. The yield of MeCS was 58.3 g. Neutral equivalent was 344.2; calc. 342.5.

The remaining ether solution was washed with water and stripped to dryness to give 63.8 g of neutral products.

Methyl Tricarboxystearate (MeTriCS)

Hydroformylated linseed methyl esters (12) were oxidized as described above. The oxidized product by GLC analysis contained 41.8% MeTriCS, 16.4% MeDiCS, 3.9% unknown, 20.9% MeCS, 21% palmitate and stearate, and 1.7% short chain products. The oxidized product (833 g) was dissolved in ether and extracted 4 times with sodium bicarbonate (25 g) in water (150 ml) and methanol (100 ml). The aqueous bicarbonate solutions were extracted twice with ether. After acidification and work-up as described above, 279.3 g MeTriCS was obtained. GLC analysis: 91.5% MeTriCS, 2.5% MeDiCS, 2% stearate, and 2%

short-chain acids. Neutral equivalent was 158; calc. for MeTriCS 143.3

The ether solution containing the remaining acidic and neutral products was extracted further with aqueous sodium bicarbonate and, after work-up as described above, yielded a mixture (225.4 g) of MeTriCS and MeDiCS.

Finally, extraction with sodium hydroxide yielded 212.9 g MeCS (75.8% pure). The ether solution contained 96.3 g neutral products.

Alkyl Mono-, Di-, and Tricarboalkoxystearates

Di-, tri-, and tetraesters of branched stearic acid were prepared by transesterification-esterification of MeCS, MeDiCS, and MeTriCS with 15 mole excess of the appropriate alcohol and 2% sulfuric acid catalyst. Water was removed by azeotropic distillation with benzene. After addition of aqueous sodium bicarbonate, the products were isolated as described for Dmp-ME diester. Distillation gave the desired alkyl-alkyl diesters (10). EtHex-EtHex diester also was prepared in 92% yield from Me-Me diester by alkaline transesterification with EtHex-OH (Table I).

Bu-DiBu triester was passed through a falling film still, and a fraction boiling at 230-238 C (0.07 mm) was collected. Analysis: Calc. for $C_{32}H_{60}O_6$: C, 71.06; H, 11.18. Found: C, 70.62; H, 11.09.

Bu-TriBu tetraester was passed through a falling film still, and a fraction boiling 265-270 at 0.025 mm was collected. Analysis: Calc. for $C_{37}H_{68}O_8$: C, 69.33; H, 10.69. Found: C, 69.05; H, 10.47.

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