Acetoxyglycerol Acetal Derivatives of Mono- and Polyformyloctadecanoate Esters: Plasticizers for Poly(Vinyl Chloride)

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ABSTRACT

Methyl and butyl(acetoxyglycerol acetal) esters were prepared from 9(10)-formyloctadecanoate or its dimethyl acetal. Mixtures of acetoxy mono- and diglycerol acetals, plus acetoxy mono-, di-, and triglycerol acetals, were prepared respectively from hydroformylated safflower and linseed methyl esters. The glycerol acetals were characterized with respect to physical, thermal, chromatographic, and spectroscopic properties. Acetoxy-mixed glycerol acetals from safflower and linseed methyl esters were good primary plasticizers for poly(vinyl chloride) (PVC), whereas acetoxyglycerol acetals of hydroformylated methyl and butyl oleate were good secondary PVC plasticizers. As primary plasticizers, the poly(acetoxyglycerol acetal) esters showed less migration, better

heat stability, and higher tensile strength than the generally used PVC plasticizer di(2-ethylhexyl) phthalate.

INTRODUCTION

The plasticizer di(2-ethylhexyl) phthalate (DOP), extensively used for poly(vinyl chloride) (PVC), is now found in animal or human tissues and the environment (1-5). DOP pervasiveness emphasizes the need for plasticizers which do not easily extract, migrate, or volatilize from PVC. DOP has an LD_{50} oral toxicity (rat) of 30 mg/kg body wt compared to 1280 mg/kg for di(2-ethylhexyl) or dioctyl sebacate (DOS), a less permanent PVC plasticizer (6). Also, plasticizers are needed that are derived from renewable agricultural sources rather than being petroleum based (7).

Various plasticizer candidates have been investigated at the Northern Laboratory from derivatives made by the hydroformylation of unsaturated fatty esters. Methyl oleate was selectively hydroformylated in the 9-double bond position by a new procedure based on rhodium triphenylphosphine catalyst (8). The product, 9(10)-formyloctadecanoate, was converted to a series of acetal-esters. Although these acetal-esters were not sufficiently compatible with PVC to be primary plasticizers, they were useful as secondary plasticizers (9). Since then, primary PVC plasticizers have been made from molecularly distilled di- and triethylene and dimethyl acetals of selectively hydroformylated safflower, soybean, and linseed oil methyl esters (10). Compared to DOP, these triacetals showed less migration; equivalent volatility, compatibility, and strength; but inferior low temperature and heat stability.

We prepared and characterized mono- and poly(acetoxyglycerol acetals) from hydroformylated oleate and vegetable oil methyl esters and evaluated them as PVC plasticizers.

EXPERIMENTAL PROCEDURES

Reagents

Formyl derivatives of methyl and butyl oleate were prepared by selective hydroformylation (8) and the methyl formyloctadecanoate dimethyl acetal by direct H_2SO_4-catalyzed acetalation of the aldehyde in methanol-dimethoxypropane (9). Methyl palmitate and stearate were removed as urea adducts from methyl formyloctadecanoate dimethyl acetal. The dimethyl acetal was not distilled. Preparation of polyformyl derivatives from methyl esters of safflower and linseed oils was previously reported (11,12). Glycerol (ACS certified, Fisher Scientific Co., Fairlawn, NJ), 1,4-dioxan, peroxide free (Fisher, purified), acetic anhydride (Fisher, ACS certified), and sulfuric acid (ACS reagent, Allied Chemical, Morristown, NJ) were used as received.

Analytical Methods

Gas-liquid chromatography (GLC) was performed as previously described (9) except for a temperature program of 180-270 C at 4 C/min and 16 min upper temperature hold. Hydroxy samples were converted to suitable deriva-
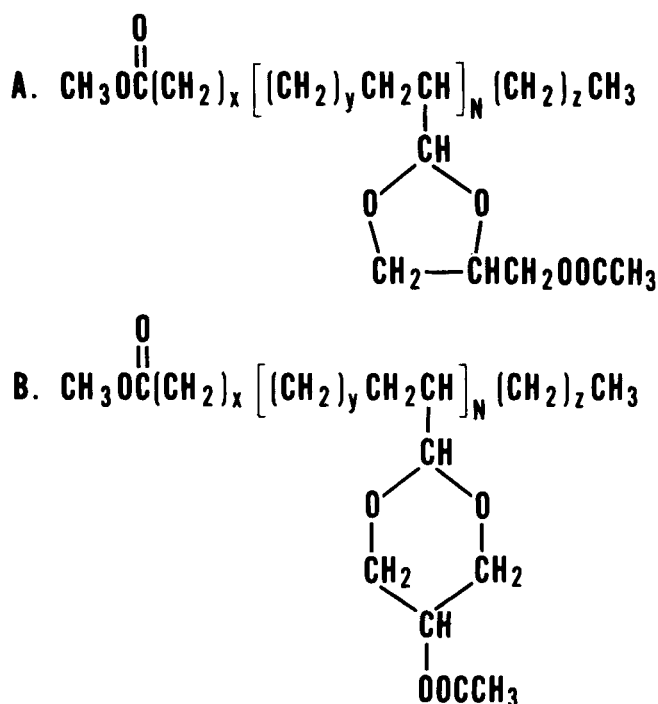
FIG. 1. Acetoxyglycerol acetal derivatives of mono- and polyformyl stearates. (A) Five-membered ring isomers: methyl 9(10)-[2-(4-ethanoyloxymethyl-1,3-dioxolanyl)]octadecanoate (N = 1, y = 0, x + z = 14); methyl 9(10), 12(13)-bis[2-(4-ethanoyloxymethyl-1,3-dioxolanyl)]octadecanoate (N = 2, y = 1, x + z = 10); methyl 9(10), 12(13), 15(16)-tris[2-(4-ethanoyloxymethyl-1,3-dioxolanyl)]octadecanoate (N = 3, y = 1, x + z = 7). (B) Six-membered ring isomers: methyl(butyl) 9(10)-[2-(5-ethanoyloxy-1,3-dioxanyl)]octadecanoate (N = 1, y = 0, x + z = 14); methyl 9(10), 12(13)-bis[2-(5-ethanoyloxy-1,3-dioxanyl)]octadecanoate (N = 2, y = 1, x + z = 10); methyl 9(10), 12(13), 15(16)-tris[2-(5-ethanoyloxy-1,3-dioxanyl)]octadecanoate (N = 3, y = 1, x + z = 7).

TABLE I

Analytical and Physical Properties of Acetoxyglycerol Acetal Esters

Characteristics	Acetoxyglycerol acetal		Poly(acetoxyglycerol acetal)	
	Methyl octadecanoate	Butyl octadecanoate	Safflower oil methyl esters	Linseed oil methyl[a] esters
GLC (% by wt)[b]				
Palmitate	0.0	0.0	8.2	6.4
Stearate	0.0	2.3	3.3	4.3
Monoacetal	99.0	97.7	26.5	19.3
Diacetal	---	---	62.0	23.2
Triacetal	---	---	---	46.8
TLC (R_f)[b]				
Monoacetal	0.48	0.51	0.48	0.48
Diacetal	---	---	0.37	0.37
Triacetal	---	---	---	0.24
Acid value	1.7	1.4	2.8	3.4
Hydroxy value[c]	2.9	1.8	0.9	7.2
Elemental analysis				
Carbon (%)				
Calculated	67.67	69.22	---	---
Found	67.82	68.84	---	---
Hydrogen				
Calculated	10.70	11.02	---	---
Found	10.78	10.78	---	---
Physical properties				
Mp (c)[b]	-76.0	-83.0	-53.6	-21.4
N_D^{20}	1.4595	1.4642	1.4666	1.4724
d_{20}^{20}	0.9919	0.9855	1.0380	1.0730
Mol wt[d]				
Calculated	444	483	513	593
Found	434	476	501	588
Molecular refractivity[e]				
Found	122.39	136.06	---	---
Calculated	122.27	136.21	---	---

[a]Gas-liquid chromatography (GLC) of hydroformylated methyl linseed oil.

[b]GLC, thin-layer chromatography (TLC), and melting points (Mp) detailed in Experimental Procedures.

[c]AOAC Tentative Method Cd 13-60 (18).

[d]Saponification equivalents.

[e]Lorenz and Lorentz equation and compound structure (19) from Chapter XI of Vogel *Practical Organic Chemistry*.

tives for GLC by acetylation or silylation (13).

Thin layer chromatography (TLC) was carried out on precoated silica gel plates (F-254, 0.25-mm thickness; E. Merck, Darmstadt, W. Germany) with a 10% petroleum ether:90% diethyl ether solvent system.

Melting points were determined by thermal mechanical analysis as previously reported for polymer softening points except the stage was coated with sample and the probe load was 1.0 g (13). Thermogravimetric procedures were followed as reported earlier (13).

Synthesis

Methyl(glycerol acetal) octadecanoate—Method A (direct acetalation): A mixture of methyl 9(10)-formylocta-decanoate (35.7 g, 91.7%, 0.1 mol), glycerol (9.6 g, 5% excess), 1,4-dioxan (100 ml), and concentrated H_2SO_4 (0.2 ml) was stirred and heated to 100-120 C with azeotropic removal of water at vapor temperatures of 88.5-97.0 C for 5 hr. The reaction mixture was cooled to room temperature, neutralized with anhydrous NaOAc, transferred with Et_2O to a separatory funnel, washed carefully with dilute $NaHCO_3$, and then washed with saturated NaCl solution. A saturated NaCl solution was required to avoid troublesome emulsions. The washings were extracted with Et_2O two times. All Et_2O portions were dried over anhydrous $MgSO_4$ and stripped to give a yellow product (39.8 g; theor: 45.0 g; N_D^{20} 1.4688). GLC of the trimethyl-

silyl (TMS) derivative showed 89.3% acetal, 10.7% saturated methyl esters, and 0% aldehyde.

Method B (transacetalation): A mixture of methyl 9(10)-dimethoxymethyloctadecanoate (186 g, 99%, 0.5 mol), glycerol (48.4 g, 5% excess), and concentrated H_2SO_4 (0.2 ml) was stirred and heated to 110-114 C at 13-14 mm Hg for 5 hr. The distillate (32 g methanol) was collected in a dry-ice trap. Flask contents were washed with Et_2O into a separatory funnel followed by washing with dilute $NaHCO_3$ and then saturated NaCl solution. The Et_2O layer was dried over anhydrous $MgSO_4$, filtered and stripped to give a light yellow product (192 g; theor: 200 g; N_D^{20} 1.4659). GLC of the TMS derivative showed 99% acetal, 1% methylstearate, and 0% dimethyl acetal.

Other glycerol acetal octadecanoates: Butyl(glycerol acetal) octadecanoate (92.6% crude yield, 97.0% glycerol acetal by GLC, N_D^{20} 1.4735) and poly(glycerol acetal) octadecanoate derivatives of safflower oil methyl esters (96.2% crude yield, N_D^{20} 1.4754) and of linseed oil methyl esters (90.5% crude yield, N_D^{20} 1.4838) were prepared by Method A.

IR (neat) of glycerol acetals: 3700-3100 (OH), 2920-2850 (CH_3 and CH_2), 1740 (ester C=O), 1155 (ester C-O-C), 1194 (ester and acetal C-O-C), 1110, 1038, 975 cm^{-1} (acetal C-O-C).

Acetoxyglycerol acetals: Butyl(glycerol acetal) octadecanoate (139 g, 97%, 0.3 mol), 300 ml acetic anhydride, and

TABLE II

Thermogravimetry of Glycerol Acetal Esters and Commercial Plasticizers

Compound	T_i (C)[a]	T_{10} (C)[a]	Rate (mg/C x 10^{-2})[b]
Acetoxyglycerol acetal			
Methyl octadecanoate	160	236	5.0
Butyl octadecanoate	169	238	14.0
Poly(acetoxyglycerol acetal)			
Safflower oil methyl esters	127	217	15.6
Linseed oil methyl esters	122	225	3.7
DOP[c]	147	205	19.0
DOS[c]	132	220	20.0

[a]T_i is the temperature for initial wt loss; T_{10}, at 10% wt loss.

[b]Wt loss rates are measured from linear regions of the thermogravimetric curve.

[c]DOP = di(2-ethylhexyl) phthalate, DOS = di(2-ethylhexyl) sebacate.

0.1 ml concentrated H_2SO_4 were refluxed for 0.5 hr. Excess acetic anhydride and acetic acid were removed on a rotary evaporator at 80 C and 0.3 mm Hg vacuum. The product was diluted with Et_2O and washed with dilute $NaHCO_3$ followed by distilled H_2O. Et_2O solution was dried over anhydrous $MgSO_4$ and stripped to give a dark yellow product (147 g, 98.0% crude yield, 97.0% acetoxy acetal, no free OH by GLC, IR (neat): no hydroxyl absorption at 3700-3100 cm⁻¹, 1230 cm⁻¹ (strong acetoxy absorption).

Color Removal

The acetoxyglycerol acetals were bleached as follows: A petroleum ether solution of 85 g dark yellow 99% methyl-(acetoxyglycerol) octadecanoate was passed under N_2 pressure through a column of 25 g of a 1:1 mixture of Celite and activated carbon (ICI United States Inc., Wilmington, DE). Elution with additional petroleum ether gave 78.3 g of a light yellow product.

Plasticizer Evaluations

All test procedures were reported previously (14,15).

RESULTS AND DISCUSSION

Characterization

Glycerol acetals were prepared either by direct acetalation of methyl 9(10)-formyloctadecanoate with glycerol or by transacetalation of methyl 9(10)-dimethoxymethyloctadecanoate. In either method a mixture of five-membered (hydroxymethyldioxolanyl) and six-membered (hydroxydioxanyl) rings is formed. Acetylation of the free hydroxyl groups readily produced the acetoxymethyldioxolanyl (Fig. 1A, N = 1) and acetoxydioxanyl (Fig. 1B, N = 1) fatty esters.

The reaction sequence with direct acetalation was extended to hydroformylated safflower and linseed fatty esters. In addition to methyl palmitate, stearate, and monoacetal, the product from safflower oil contained diacetals (Fig. 1A and B, N = 2); the product from linseed oil contained triacetals (Fig. 1A and B, N = 3).

Evidence for five- and six-membered ring structures is based on NMR ($CDCl_3$, tetramethylsilane), which showed doublets at 4.85-4.78 and 4.52-4.44 ppm for the methine acetal proton on the respective five- and six-membered rings (16). From the ratio of the five- to six-membered ring protons, the five-membered ring was estimated at 70-80%. Also present is resonance (4.10-3.99 ppm) for protons of the methylene group attached to the acetate oxygen and adjacent to the five-membered ring (Fig. 1A). Additional NMR data support the acetoxyglycerol acetal ester structures in Figure 1: δ 3.55-3.67 (s, CH_3CO), 2.22-2.29 (m, -CH_2CO_2R), 1.98-2.08 (s, CH_3CO_2), 1.28-1.32 (s, -CH_2),

and 0.88-0.89 ppm (m, CH_3-).

Mass spectral analysis confirmed structure of Figure 1 for methyl acetoxyglycerol acetal octadecanoate; (70 ev) m/e (fragment, relative intensity in percent): 441 (M - 3, 1.97), 410 (441 - 31, CH_3O, 7.93), 145

$$(CH\underset{O}{\overset{O}{\diagdown}}\underset{CHCH_2OCOCH_3}{\overset{CH_2}{\diagup}}$$

99.99), 43 ($CH_3C=O$, 77.47).
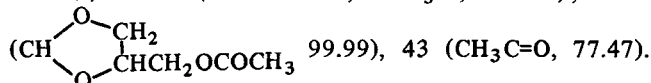
Although fragment mass 145 corresponds to the glycerol acetal ring substituent, this evidence cannot be used to establish whether we have a five- or six-membered ring.

Structures of these ester-acetals are further supported by IR (neat): 1110, 1045, 1020, 975 (acetal C-O-C), 1190 (acetal-ester C-O-C), and 1155 (ester C-O-C), 1740 (ester C=O), and 2920-2850 cm⁻¹ (C-H). IR was particularly useful to indicate completeness of acetylation by the disappearance of the free glycerol hydroxy absorption 3700-3100 cm⁻¹ and the appearance of the intense acetoxy group absorption at 1230 cm⁻¹. Hydroxy contents too small to be detected by IR were analyzed chemically (Table I).

When mono-, di-, and triformyl C-18 alkyl-ester products of safflower and linseed oil methyl esters (11,12,17) were acetalated with glycerol and then the free OH acetylated, GLC analysis showed the formyl components disappearing and new components having peaks with longer retention times appearing. The chromatograms for poly(acetoxyglycerol acetals) were complex and resembled those obtained previously for the dimethyl and ethylene glycol acetals of hydroformylated safflower and linseed oil methyl esters (10). Chromatograms of mono(acetoxyglycerol acetal) and di(acetoxyglycerol acetal) components showed retentions represented by two and four peaks, respectively. The tri(acetoxyglycerol acetal) was not sufficiently volatile to emerge from the gas chromatograph. Fatty ester and acetal compositions determined by GLC are given in Table I.

TLC showed decreasing R_f values for the mono-, di-, and tri(acetoxyglycerol acetals) components (Table I). Elemental analyses, mol wts, and refractivities (Table I) are in agreement with calculated values for acetoxyglycerol acetal structures shown in Figure 1.

Thermal Analysis

The stabilities of acetoxyglycerol acetal plsticizers were compared with those of the commercial plasticizers DOP and DOS (Table II). DOP and DOS began to lose wt initially at temperatures lower than the mono(acetoxyglycerol acetals) but at temperatures higher than the poly(acetoxyglycerol acetals). However, both the mono- and poly(acetoxyglycerol acetals) showed slower wt loss than DOP as exhibited by the temperatures for 10% wt loss and by the rate of wt loss (Table II). These latter results

TABLE III

Mechanical Properties of Plasticized Polyvinyl Chloride

Plasticizer	Torsional stiffness (C)		Compatibility (Δ)	Migration wt loss (%)	Volatility wt loss (%)	Heat stability (hr)	Tensile strength (psi)	Elongation (%)	100% Modulus (psi)
	T_f	T_4							
Primary, 32%									
Acetoxyglycerol acetal									
Butyl octadecanoate	-31	25	56	11.2[a]	9.4	7	2550	190	1715
Poly(acetoxyglycerol acetal)									
Safflower oil methyl esters	-14	23	37	1.6	3.2	9	2935	275	2030
Linseed oil methyl esters	-1	29	30	0.04	2.0	8	3005	240	2430
DOP[b]	-25	4	29	3.0	1.5	6.5	2835	290	1165
DOS[b]	-57	-7	50	19.3	1.6	---	2355	295	1045
Secondary, 50:50 DOP 32%									
Acetoxyglycerol acetal									
Methyl octadecanoate	-27	11	38	5.7	1.3	10	2805	210	1590
Butyl octadecanoate	-30	8	38	5.9	1.1	9	2830	365	1425
Poly(acetoxyglycerol acetal)									
Safflower oil methyl esters	-20	11	31	2.3	1.4	10	2870	330	1560
Linseed oil methyl esters	-13	15	28	1.3	1.0	9	2875	285	1670
DOP:DOS	-43	-5	38	12.2	1.5	---	2790	290	1150

[a]Exudate overnight.
[b]DOP = di(2-ethylhexyl) phthalate, DOS = di(2-ethylhexyl) sebacate.

correlate with the heat stability results given for these same plasticizers in Table III.

Plasticizer Evaluation

Methyl and butyl(acetoxyglycerol acetal) octadecanoates and poly(acetoxyglycerol acetal) derivatives of safflower and linseed oil methyl esters were evaluated as plasticizers for PVC (Table III).

The acetoxyglycerol acetals conformed to the previous observation that compatibility with PVC is improved, compatibility number lowered (15), with increasing number of acetal functions per ester molecule (10). The order of compatibility with PVC for the glycerol acetals as primary plasticizers compared to commercial plasticizers is DOP $\simeq$ poly(acetoxyglycerol acetal) linseed oil methyl esters > poly(acetoxyglycerol acetal) safflower oil methyl esters >> DOS > butyl(acetoxyglycerol acetal) octadecanoate. Compatibility for 50:50 mixtures of acetoxyglycerol monoacetal with DOP was equivalent to that of DOP:DOS 50:50 mixtures. Changing the methyl ester group to butyl produced no change in compatibility.

Butyl(acetoxyglycerol acetal) octadecanoate as a primary plasticizer has a better low-temperature property, T_f, than the poly(acetoxyglycerol acetals) and DOP, but not DOS. This observation is in accordance with the low temperature properties of the corresponding di- and tri-dimethyl and ethylene glycol acetal (10). As secondary plasticizers, the butyl ester showed no substantial improvement in low-temperature property over the methyl ester monoglycerol acetal.

Compatibility of the methyl and butyl monoacetoxy-glycerol acetals was poor at the 32% concentration required for primary plasticizers. The methyl ester did not mix completely with PVC, and tests could not be carried out that would have any meaning. The butyl ester did mix completely so that tests could be carried out, but it exuded from the PVC upon standing overnight.

Conversion of methyl polyformyloctadecanoate to the acetoxyglycerol acetal produced a plasticizer with permanence properties (migration and volatility) better than those of the di- and tri-dimethyl and ethylene glycol acetals (10). The poly(acetoxyglycerol acetals) produced less migration than DOP. As the number of acetoxyglycerol acetal functions increased per molecule, heat stability remained essentially the same, but migration wt loss decreased. Volatility wt loss for polyglycerol acetals was essentially equivalent to that of DOP and di- and tri-dimethyl and ethylene glycol acetals (10). As secondary plasticizer, the permanence properties of the butyl(acetoxy-glycerol acetal) ester were not substantially better than those of the methyl ester.

Poly(acetoxyglycerol acetal) derivatives of linseed and safflower oil methyl esters produced plasticizers of better tensile strengths than those of DOP and DOS. The acetal content of methyl(acetoxyglycerol acetal) of safflower oil is intermediate between that of the corresponding derivative of linseed and oleic methyl esters. This intermediate composition produced the best elongation, which is approximately equivalent to that of DOP. As secondary plasticizers, the safflower oil and butyl octadecanoate acetals gave better elongation than the DOP:DOS control. The butyl ester as secondary plasticizer also had better tensile strength, elongation, and modulus than methyl octadecanoate(acetoxyglycerol acetal).

A decrease in the glycerol acetal groups gave lower modulus in plasticized PVC. However, the modulus for any of the glycerol acetals was not so good as that produced by DOP.

An overall comparison shows that poly(acetoxyglycerol acetal) derivatives of safflower and linseed oil methyl esters, as primary PVC plasticizers, provide better tensile strength than the generally used DOP. Methyl and butyl(acetoxy-glycerol acetal) octadecanoates, as secondary PVC plasticizers, provide better tensile strength than the DOP:DOS. These plasticizers also have greater permanence and stability than DOP. This greater permanence would be of particular importance to minimize environmental contamination.

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