

3901*

8-9-73

Ethylene and Dimethyl Acetals from Hydroformylated Linseed, Soybe
and Safflower Methyl Esters as Plasticizers for PVC¹

R. A. AWL, E. N. FRANKEL, G. R. RISER² and E. H. PRYDE, Northern
Regional Research Laboratory,³ Peoria, Illinois 61604

Running Title: Acetal-Esters as Plasticizers for PVC

Proof to be sent to: Dr. H. J. Dutton

Northern Regional Research Laboratory

1815 North University Street

Peoria, Illinois 61604

¹ Presented at the AOCS Meeting, Chicago, Illinois, September 16-19, 1973.

² Eastern Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, Pennsylvania 19118.

³ Agricultural Research Service, U.S. Department of Agriculture.

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ABSTRACT

Methyl and ethylene acetals of polyformyl₁ unsaturated fatty esters were prepared, characterized and evaluated as polyvinyl chloride (PVC) plasticizers. Methyl acetals were prepared with trimethyl orthoformate as a water scavenger in the acid-catalyzed acetalation reaction. With ethylene acetals, water was removed azeotropically. Although the acetals prepared were mixtures, molecular distillation gave diacetal esters of 80-90% purity and triacetal esters of 80-95% purity. The samples were characterized by GLC and by IR and NMR spectroscopy. Compared to di-2-ethylhexyl phthalate (DOP) as plasticizers for PVC, the triacetal esters (both methyl and ethylene acetals) had equivalent compatibility and strength, better migration and at least equivalent volatility, but somewhat less desirable low-temperature and heat stability properties. The diacetal esters also had good compatibility, equivalent strength, somewhat better low-temperature, but less desirable migration and volatility properties.

INTRODUCTION

Because phthalate plasticizers may volatilize or be leached from plastics and accumulate in vital animal tissues, they have been suspect as ubiquitous environmental contaminants; when used indiscriminately (1). There is an increasing demand for specialty plasticizers with better permanence, compatibility, low-temperature properties and heat and light stability. Other currently desirable plasticizer properties include strength, flame retardancy, bacteria and mold resistance and, of course, low cost.

Many acetal esters can act as primary or secondary plasticizers for polyvinyl chloride (PVC); certain acetal esters derived from azelaaldehydic acid improve low-temperature properties of PVC and stabilize it (2). Recently, various acetal esters were made from methyl 9(10)-formylstearate (MFS), prepared by selective hydroformylation of methyl oleate (3). Acetals from MFS enhanced low-temperature properties of PVC as secondary plasticizers but were not sufficiently compatible to serve as primary plasticizers (4). Hydroformylations of polyunsaturated vegetable oils and esters with the selective rhodium-triphenylphosphine catalyst produced in high yield di- and triformylstearates with narrow isomeric distributions (5-7). Both di- and triacetals from these polyformyl derivatives should be effective primary plasticizers. This paper describes the preparation, properties and plasticizer evaluations of various ethylene acetals (EA) and dimethyl acetals (DMA) from hydroformylated polyunsaturated fatty esters.

EXPERIMENTAL PROCEDURE

Materials

Hydroformylated vegetable oil esters were prepared as previously reported (5,7). Ethylene glycol (Matheson, Coleman & Bell; 99+%) and trimethyl orthoformate [$\text{CH}(\text{OCH}_3)_3$, Aldrich Chemical Co.; 98+%] were used as purchased.

Analytical Methods

Acid values were determined by titration of weighed samples in a mixture of $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$ (20:40) with standard NaOCH_3 in CH_3OH to the phenolphthalein end point. Hydroxyl values were determined according to the procedure of Siggia and Hanna (8). GLC of the hydroformylated samples and their corresponding acetals was done as before (4), except that temperature programming was increased to 180-260 C at 4 C/min and helium flow, to 75 ml/min. Methods for TLC of the polyfunctional aldehyde esters and of their acetals and enol ethers were the same as described for MFS and its acetals (3). Qualitative IR and NMR spectra were also obtained by methods previously reported (3,4).

Dimethyl Acetals (DMA)

A three-necked round-bottomed flask equipped with a gas inlet tube, a stopper and a Friedrich condenser (or in later runs, a condenser with dry ice and acetone), connected to a silicone oil bubbler was purged with dry N_2 . Then 252 g of hydroformylated linseed methyl esters (Sample 2, Table I) was added to 300 ml of CH_3OH in the flask.

TABLE I

This mixture was stirred magnetically as a slow flow of N_2 was continued while 100 ml of 7% $HCl-CH_3OH$ and 133 ml $CH(OCH_3)_3$ were added before the flask was stoppered. The cloudy mixture became homogeneous and a gentle reflux began immediately after addition of $CH(OCH_3)_3$ was completed. No external heat was applied. After 2 hr, GLC analyses indicated that the acetalation was complete. The acidic solution was neutralized with 250 ml of 6% $NaHCO_3$ before the mixture was transferred to a separatory funnel. (Crude acetal is heavier than water.) After the aqueous wash was separated and extracted with CH_2Cl_2 , the crude product diluted in ether was washed three times with water. These aqueous washes were extracted with CH_2Cl_2 ; the extract was washed again and added to the ether solution. This solution was dried with $MgSO_4$ and filtered. Solvent was removed on a rotary evaporator to afford 285 g of clear, yellow liquid (Sample 2A, Table I). This crude product (281 g) was fractionated by two successive molecular distillations (Arthur F. Smith Rota-Film Molecular Still) to obtain a clear, colorless distillate (137 g, Sample 2B, Table I) which distilled at 115-125 C/36-30 millitorr. Sample 2B was distilled from the residue (164 g) of the first distillation because the first distillate (113 g; distilled at 87-98 C/35 millitorr) consisted mostly of palmitate, stearate and monoacetal.

Ethylene Acetals (EA)

Benzene (500 ml), $KHSO_4$ (5.0 g, fused and pulverized), ethylene glycol (171 ml) and hydroformylated linseed esters (500 g, Sample 6,

Table I) were added to the reaction flask and purged with dry N_2 . The acetalation apparatus was essentially the same as for the DMA except that a Dean-Stark receiver was inserted between the reaction flask and the condenser to collect benzene-water azeotrope. The mixture became homogeneous after heating to reflux temperature. After refluxing 12 hr and 53 g of water was collected, acetalation was complete as indicated by GLC. The cooled solution was decanted into a separatory funnel, the residue consisting of mostly unreacted glycol and insoluble catalyst was washed several times with benzene, and the benzene was decanted into the separatory funnel. The benzene solution was washed first with a bicarbonate solution and then with water. The work-up was essentially as described for the DMA. A clear, amber liquid was obtained (614 g, Sample 6A, Table I). This crude acetal (553.5 g) was subjected to five successive molecular distillations to produce a clear, colorless distillate (206-219 C/30-35 millitorr; 110.8 g, Sample 6B, Table I) which analyzed 95% triacetal by GLC.

Acetal 8A of Table I was prepared from distilled safflower DMA (acetal 8, Table I) by the transacetalization procedure of Pryde et al. (9,10).

Spectroscopy

In addition to the expected aliphatic methyl or methylene IR absorptions, characteristic bands were observed. Intensities are indicated as s (strong), m (medium or moderately), w (weak)

and sh (shoulder). Analyses (neat) for the DMA showed: 2980-2975 cm^{-1} sh m (ν_a for acetal CH_3O); 2825-2820 cm^{-1} m (associated acetal CH_3O); 1740-1735 cm^{-1} s (ester $\text{C}=\text{O}$); 1415 cm^{-1} sh w (acetal CH_3O); 1240 cm^{-1} mw and 1165 cm^{-1} m (ester $\text{C}-\text{O}-\text{C}$); 1190-1180 cm^{-1} s (ester and acetal $\text{C}-\text{O}-\text{C}$); 1103 cm^{-1} s, 1068 cm^{-1} s, 1050 cm^{-1} s, 1022 cm^{-1} m and 955 cm^{-1} m (acetal $\text{C}-\text{O}-\text{C}$). IR analyses (neat) for the EA showed: 2760 cm^{-1} w (overtone); 1740-1735 cm^{-1} s (ester $\text{C}=\text{O}$); 1396 cm^{-1} m ($\text{O}-\text{CH}_2\text{CH}_2-\text{O}$ in-plane deformation); 1250 cm^{-1} sh mw, 1195 cm^{-1} m and 1155-1148 cm^{-1} m (ester $\text{C}-\text{O}-\text{C}$); 1105 cm^{-1} s, 1130 cm^{-1} m, 960 cm^{-1} sh m and 940 cm^{-1} m (acetal $\text{C}-\text{O}-\text{C}$).

NMR resonances (CDCl_3) present in DMA but absent in EA spectra were (s = singlet, m = multiplet): δ 3.30(s) for $(\text{CH}_3\text{O})_2\text{CH}-$; δ 3.40(m) for $-\text{CH}-\text{CH}\begin{matrix} \text{O}- \\ | \\ \text{O}- \end{matrix}$; δ 4.10 (either a broad doublet with the triacetals or a doublet of a doublet with the diacetals for $-\text{CH}-\text{CH}\begin{matrix} \text{O}- \\ | \\ \text{O}- \end{matrix}$; and unidentified, broad singlets at δ 4.40 and δ 4.62 with the triacetals but not the diacetals. Proton resonances seen only in the EA spectra were at δ 3.62(m) for $-\text{OCH}_2\text{CH}_2\text{O}-$ and at δ 4.73 for $-\text{CH}-\text{CH}\begin{matrix} \text{O}- \\ | \\ \text{O}- \end{matrix}$ as either a broad singlet for the triacetals or as a doublet for diacetals.

NMR spectral variations resulted from di- and trisubstitutions on the stearate moiety. The multiplet at δ 1.55 for methylenes beta to the ester group became less distinct in spectra of the tri-DMA. In spectra of the EA samples, this resonance overlapped considerably with the resonance at δ 1.26 for chain methylenes. The resonance for terminal CH_3- at δ 0.88 was a triplet for all the spectra but those of

the linseed EA. NMR spectra of EA samples 6B and 7B (Table I) showed a multiplet at δ 0.88. Several weak unidentified resonances at δ 7.15 and δ 7.33 were observed in some of the aldehyde ester spectra but not in their acetal spectra.

Plasticizer Evaluations

Test procedures and formulations were essentially the same as reported previously (2,11).

RESULTS AND DISCUSSION

Hydroformylated methyl esters from linseed, soybean and safflower oils were readily converted to mixtures of polyfunctional acetal esters to produce specialty PVC plasticizers. The fractionally distilled EA and DMA were clear, colorless liquids, which were partially characterized chromatographically and spectroscopically.

Because crude, hydroformylated methyl esters rapidly convert to DMA with $\text{CH}(\text{OCH}_3)_3$ and HCl in CH_3OH solution under ambient conditions, oxidation and other reactions are minimized. Any carboxylic acid impurities also convert to methyl esters. Table I summarizes analyses of aldehyde esters, as well as of the crude and the distilled polyfunctional acetal esters that were evaluated as plasticizers. All the DMA, except sample 5A, were prepared with the $\text{HC}(\text{OCH}_3)_3$ -HCl- CH_3OH solution. An attempt was made to acetalate sample 5 in $\text{CH}_3\text{OH}-(\text{C}_2\text{H}_5)_2\text{O}$ at reflux with a strong acidic cation exchange resin by an adaptation of the method of Beal et al. (12). However under the conditions of this method, acetalation proved too

sluggish and was driven to completion finally with $\text{CH}(\text{OCH}_3)_3$ and p-toluenesulfonic acid.

For good PVC plasticizer compatibility, free acid should be less than 1-2%. The acid values in Table I, generally quite low, show that little oxidation of aldehyde esters occurred. The only significant increases in acidity with acetalation are shown by EA samples 7A and 8A that required more vigorous acetalation conditions, resulting in oxidation.

For good compatibility with PVC, plasticizers should also have low hydroxyl content. Several aldehyde esters were analyzed for hydroxyl value (Table I, see footnotes) with the pyromellitic dianhydride (PMDA)-pyridine reagent of Siggia and Hanna (8) because aldehydes interfere with the standard acetic anhydride-pyridine reagent. Although the aldehyde esters gave relatively low hydroxyl values, the PMDA reagent was unsuited for analyzing the acetal esters. High and erratic values result when ethyl azelaaldehyde diethyl acetal (13) was used as a standard even though it was free of hydroxyl groups according to GLC, TLC and IR. Hydroxyl values determined for various acetal esters also were not reproducible. However, IR spectra showed little or no hydroxyl impurities in these acetals. More hydroxyl impurity was indicated for EA samples 7A, 7B and 8A than for the other acetals of Table I. An NMR spectrum of sample 7B showed a broad and very shallow resonance at δ 4.08 to 4.30 suggesting trace hydroxyl impurity. None of the acetal esters

in Table I showed as much hydroxyl impurity according to IR as did their aldehyde esters. The bicarbonate and aqueous washes during work-up of the crude acetals would be expected to remove some hydroxyl impurities.

In addition to the slight hydroxyl impurity in EA samples 7B and 8A, IR analyses indicated weak absorptions at 1810 cm^{-1} which suggested trace or minor amounts of cyclic anhydride.

Chromatography

Gas-liquid chromatograms showing separations between palmitate and stearate, formylolate and formylstearate, and the di- and the tri-formylstearates have been reported earlier (5). The complexity of samples in Table I is illustrated by representative chromatograms from crude, hydroformylated linseed methyl esters; their crude acetals and distilled fractions (Figures 1 and 2). The discrepancy between

FIGS. 1 and 2

GLC analyses for aldehyde esters and for corresponding unsaturated fatty esters is attributed to incomplete hydroformylation and carbon-carbon double bond hydrogenation observed with polyunsaturates but not with monounsaturates (5,7).

Although slight overlapping of peaks due to di- and tri-formyls with peaks due to corresponding acetals is indicated in Figures 1 and 2, the respective acetal peaks, in general, display longer retention times. The di-DMA esters as a group exhibited a characteristic

aggregation of peaks. Di-DMA from hydroformylated safflower, soybean or linseed esters consistently exhibited four large peaks together with several small, partially resolved peaks or shoulders. The triacetal esters gave also a characteristic aggregation of peaks. Some fractionation of the di- and the tri-acetal groups of isomers was apparent after successive distillations. A chromatogram of the highly distilled sample 1B with that of crude acetal sample 1A, for example, shows that peaks with lower retention times in either group diminished in size and area compared to the later peaks. Fractionation of isomers was not so obvious in the chromatograms of samples EA 6A and 6B (Fig. 2).

Since acyclic aliphatic acetals, particularly DMA, are prone to undergo cracking to enol ethers when heated, distilled or chromatographed (4,10), it was important to detect any possible enol ether impurities. To obtain standards, polyfunctional enol ethers were prepared from the safflower and linseed DMA by the method for the monoethers (4). Polyfunctional enol ethers were easily detected by TLC, exhibited higher R_f values than their DMA precursors and were in a region relatively free of any other compounds. GLC of these ether samples also showed distinct changes in the chromatograms as compared to those of the precursor acetals. Additional peaks appeared with slightly higher retention times, but these peaks showed considerable overlap with those of the starting acetals. However, the enol ethers

could be easily detected also by IR and NMR, and no chromatographic or spectroscopic evidence for their presence was found in any of the samples of Table I.

Plasticizer Evaluations

The tri-DMA and tri-EA show good compatibility and permanence as primary PVC plasticizers but do not improve low-temperature properties. This behavior is in contrast to the monoacetal derivatives previously reported (4), which had less compatibility and which could be used only as secondary plasticizers. A 50:50 combination of the monoacetals with DOP (see Formulation II of Table II) compared favorably with a

TABLE II

50:50 mixture of di-2-ethylhexyl sebacate (DOS) with di-2-ethylhexyl phthalate (DOP) at a 32% plasticizer level. The diacetal samples exhibit plasticizer properties intermediate between those for the tri- and mono-acetals.

In general, tensile strengths, elongations and 100% moduli for PVC plasticized with the di- and tri-acetals are comparable to those found with the plasticizer controls. The data of Table II indicate that the di- and tri-acetals, if used as primary plasticizers, should contain less than 9% monoacetals; otherwise, there is a significant exudate. Compared to DOP, the methyl triacetal ester (sample 1B, Table II) had superior migration and volatility properties. The ethylene triacetal ester (sample 6B) had superior migration and

equivalent volatility. The methyl diacetal esters (samples 4B, 5C) and ethylene diacetal esters (sample 8A) had slightly higher volatility. The methyl diacetal ester, but not the ethylene diacetal ester, had higher migration properties. Compared to a 50:50 combination of DOS and DOP, all 50:50 combinations of acetal esters with DOP had considerably lower migration but comparable volatility.

Heat stabilities of PVC plasticized with these acetal esters were lower than those of the control plasticizers. Since cyclic acetals are known to be more stable than DMA (4,10), it is surprising that no difference was found in heat stabilities between the DMA and the EA samples. Some structural determinant other than the acetal group, such as the alkyl ester group or the tertiary hydrogens alpha to the acetal group, could be an important factor in influencing heat stability. More research is needed to determine if stability of these acetal plasticizers can be improved by changes in ester functionality or in formulation.

ACKNOWLEDGMENTS

NMR by D. Weisleder; assistance with GLC, TLC and IR by F. L. Thomas and W. E. Neff.

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TABLE I
Hydroformylated Vegetable Oil Methyl Esters
and Their Acetals: Analyses

No.	Sample Description ^a	Acid value	Fatty esters ^b	GLC analysis, %			Other components
				Formyl/acetal			
				Esters			
Mono	Di	Tri					
1	M HF Ls ^c	6.4	14.2	27.5	24.7	33.5	0.1
1A	M HF Ls DMA	2.1	11.6	22.4	16.1	45.4	4.5
1B	1A distilled 5X	2.9	0.0	0.0	7.6	92.1	0.3
2	M HF Ls	8.5	14.2	27.0	23.5	35.3	0.0
2A	M HF Ls DMA	1.6	12.8	23.5	15.3	47.6	0.8
2B	2A distilled 2X	2.0	0.0	4.2	16.3	79.4	0.1
3	M HF Ls	2.3	10.0	22.2	22.5	43.6	1.7
3A	M HF Ls DMA	0.3	8.7	21.6	14.2	52.2	3.3
3B	3A distilled 2X	0.4	0.0	6.0	17.0	75.0	2.0
4	M HF So ^d	5.8	15.8	29.2	50.0	4.6	0.4
4A	M HF So DMA	0.7	14.4	25.2	51.9	4.5	4.0
4B	4A distilled 5X	1.3	0.0	4.0	78.0	13.0	5.0
5	M HF Sf	---	11.6	18.1	66.5	---	3.8
5A	M HF Sf DMA	2.3	7.0	12.7	77.1	---	3.2
5B	5A distilled 2X	2.6	0.5	9.3	85.1	---	5.1
5C	5B (reacetalated)	1.2	0.0	9.0	87.0	---	4.0

continued--

TABLE I.--Continued

No.	Sample Description ^a	Acid value	Fatty esters ^b	GLC analysis, %			Other components
				Formyl/acetal			
				Esters			
			Mono	Di	Tri		
6	M HF Ls ^e	8.7	14.3	27.8	23.1	34.5	0.3
6A	M HF Ls EA	6.3	11.4	24.5	19.6	43.7	0.8
6B	6A distilled 5X	7.9	0.0	0.5	3.4	95.0	1.1
7	M HF Ls	2.5	7.0	21.8	19.8	51.0	0.4
7A	M HF Ls EA	12.1	9.0	27.0	20.2	42.2	1.6
7B	7A distilled 2X	11.3	0.0	14.4	26.0	59.0	0.6
8	M HF Sf DMA ^f	0.3	0.0	8.1	90.0	---	1.9
8A	M HF Sf EA ^g	0.9	0.0	12.1	83.8	---	4.1

^aM = methyl; HF = hydroformylated; Ls = linseed esters; So = soybean esters; Sf = safflower esters; DMA = dimethyl acetals; EA = ethylene glycol acetals.

^bMethyl palmitate + methyl stearate.

^cHydroxyl value: 23.0.

^dHydroxyl value: 45.7.

^eHydroxyl value: 28.7.

^fMolecularly distilled sample.

^gSample 8 transacetalated (9,10) with ethylene glycol. Product was not distilled.

VC) Sheets Containing 32% Plasticizer^a

	100% Modulus, psi	Migration, weight loss, %	Volatility weight loss, %	Heat stability (2), hr
10	1165	3.0	1.5	6.5
15	1045	19.3	1.6	---
15	1345	3.9	0.9	7.5
0	1455	1.9	0.8	4.5
15	1245	2.7	1.3	4
10	1215	2.8	1.2	4.5
10	1295	6.6	3.2	4.5
15	1190	8.2	6.6	4

I^a

inued

	100% Modulus, psi	Migration weight loss, %	Volatility weight loss, %	Heat stability (2), hr
0:50 DOP)				
0	1150	12.2	1.5	7.5
0	1155	8.8	2.1	---
5	1265	2.6	1.0	4.5
0	1170	3.0	1.5	4
5	1255	2.7	1.3	4
0	1220	4.7	1.7	4.5
0	1080	6.0	1.9	4.5
I				
0	1795	1.0	1.8	4.5
0	1450	2.4	0.9	4.5
5	1850	2.3	2.0	3

Continued

Migration, %	Modulus, psi	100% Migration weight loss, %	Volatility weight loss, %	Heat stability (2), hr
(50:50 DOP)				
345	1130	8.4	2.1	---
280	1450	1.9	0.9	4.5
300	1225	2.5	1.4	4.5
315	1155	4.0	1.5	4

Plasticizer, 32; G62 (an epoxy plasticizer stabilizer), 1; Mark M

1) gave 3 X 6 X 0.075 in. PVC test sheets.

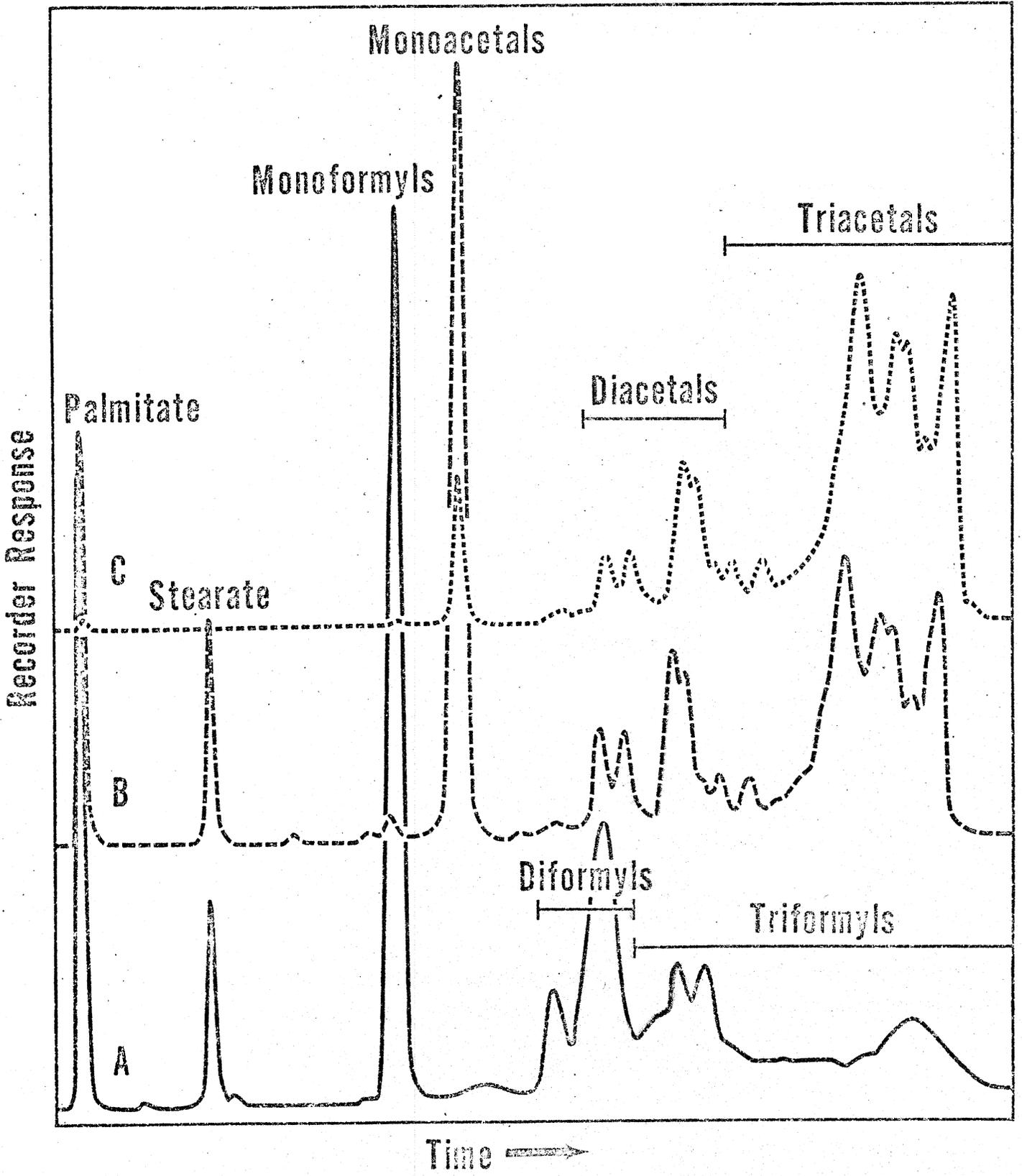
; and Plastolein 9720, a commercial polymeric plasticizer.

Plasticizer is DOP.

Figure Captions

FIG. 1. Gas-liquid chromatograms of hydroformylated linseed methyl esters and their dimethyl acetals. Curve A. — Hydroformylated linseed methyl esters (sample 2, Table I). Curve B. ---- Dimethyl acetals from the hydroformylated product of curve A (sample 2A, Table I). Curve C. Molecularly distilled acetals from the dimethyl acetals of curve B (sample 2B, Table I).

FIG. 2. Gas-liquid chromatograms of hydroformylated linseed methyl esters and their ethylene acetals. Curve A. — Hydroformylated linseed methyl esters (sample 6, Table I). Curve B. Ethylene acetals from the hydroformylated product of curve A (sample 6A, Table I). Curve C. ---- Molecularly distilled acetals from the ethylene acetals of curve B (sample 6B, Table I).



Recorder Response

