Ethylene and Dimethyl Acetals from Hydroformylated Linseed, Soybean, and Safflower Methyl Esters as Plasticizers for Polyvinyl Chloride[1]

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ABSTRACT

Dimethyl and ethylene acetals of polyformylated unsaturated fatty esters were prepared, characterized, and evaluated as polyvinyl chloride plasticizers. Dimethyl 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 gas liquid chromatography and by IR and NMR spectra. Compared to di-2-ethylhexyl phthalate as a plasticizer for polyvinyl chloride, the triacetal esters (both dimethyl and ethylene acetals) gave less migration and at least equivalent volatility characteristics; the triacetals also gave equivalent compatibility and strength, 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 (1,2). There is an increasing demand for specialty plasticizers with better permanence, compatibility, low temperature properties, strength, and heat stability. Other currently desirable plasticizer properties (not investigated here) include light stability, flame retardancy, bacteria, and mold resistance.

Many acetal esters can act as primary or secondary plasticizers for polyvinyl chloride (PVC); certain acetal esters derived from azelaldehydic acid improve low temperature properties of PVC and stabilize it (3). Recently, various acetal esters were made from methyl 9(10)-formylstearate (MFS), prepared by selective hydroformylation of methyl oleate (4). Acetals from MFS enhanced low temperature properties of PVC as secondary plasticizers but were not sufficiently compatible to serve as primary plasticizers (5). Di- and triformylstearates with narrow isomeric distributions were produced in high yield by hydroformylations of polyunsaturated vegetable oils and esters with the selective rhodium-triphenylphosphine catalyst (6-8). Both di- and triacetals from these polyformyl derivatives should be effective primary plasticizers. This article describes the preparation, properties, and plasticizer evaluations of various ethylene acetals (EA) and dimethyl acetals (DMA) from hydroformylated polyunsaturated fatty esters.

EXPERIMENTAL PROCEDURES

Materials

Hydroformylated vegetable oil esters were prepared as previously reported (6,8). Ethylene glycol (Matheson, Coleman & Bell, Norwood, Ohio; 99+%) and trimethyl orthoformate $CH(OCH_3)_3$, (Aldrich Chemical Co., Milwaukee, Wisc.; 98+%) were used as purchased.

Analytical Methods

Acid values were determined by titration of weighed samples in a mixture of CH_3OH-C_6H_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 (9). Carbonyl values were determined by a slight modification of Siggia's method (10). Acetals are hydrolyzed to aldehydes and are not distinguished by this method. Gas liquid chromatography (GLC) of the hydroformylated samples and their corresponding acetals was done as before (5), except that temperature programing was increased to 180-260 C at 4 C/min and helium flow to 75 ml/min. Methods for thin layer chromatography (TLC) of the polyfunctional aldehyde esters and of their acetals and enol ethers were the same as described for MFS and its acetals (4). Qualitative IR and NMR spectra also were obtained by methods previously reported (4,5).

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 hydroformylated linseed methyl esters (Sample 2, Table I) were added to 300 ml CH_3OH in the flask. This mixture was stirred magnetically as a slow flow of N_2 was continued, while 100 ml 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 6% $NaHCO_3$ before the mixture was transferred to a separatory funnel. 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 combined aqueous washes were extracted with CH_2Cl_2; the CH_2Cl_2 extract was washed 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 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 387-98 C/35 millitorr) consisted mostly of palmitate, stearate, and

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TABLE I

Hydroformylated Vegetable Oil Methyl Esters and Their Acetals: Analyses

			Gas liquid chromatographic analysis, %				
	Sample	Acid	Fatty	Formyl/acetal esters			Other
No.	Description[a]	value	esters[b]	Mono	Di	Tri	components
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
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

[a] M = methyl, HF = hydroformylated, Ls = linseed esters, So = soybean esters, Sf = safflower esters, DMA = dimethyl acetals, and EA = ethylene glycol acetals.

[b] Methyl palmitate + methyl stearate.

[c] Hydroxyl value: 23.0.

[d] Hydroxyl value: 21.7.

[e] Hydroxyl value: 28.7.

[f] Molecularly distilled sample.

[g] Sample 8 transacetalated (11,12) with ethylene glycol. Product was not distilled.

monoacetal.

Butyl esters were prepared from the distilled DMA-methyl esters by transesterification (5).

EA

Benzene (500 ml), $KHSO_4$ (5.0 g, fused and pulverized), ethylene glycol (171 ml), and hydroformylated linseed methyl 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. During a 12 hr reflux, 53 g water was collected; and complete acetalation was achieved as indicated by GLC. The cooled solution was decanted into a separatory funnel, the residue, consisting mostly of 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 a molecular distillation followed by four redistillations 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.

Ethylene acetal 8A of Table I was prepared from distilled safflower DMA (acetal 8, Table I) by the transacetalation procedure of Pryde, et al. (11,12).

Spectroscopy

In addition to the expected aliphatic methyl or methylene IR absorptions, the following 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 C=O); 1415 cm^{-1} sh w (acetal CH_3O); 1240 cm^{-1} mw and 1165 cm^{-1} m (ester C-O-C); 1190-1180 cm^{-1} s (ester and acetal C-O-C); 1103 cm^{-1} s, 1068 cm^{-1} s, 1050 cm^{-1} s, 1022 cm^{-1} m, and 955 cm^{-1} m (acetal C-O-C). IR analyses (neat) for the EA showed: 2760 cm^{-1} w (overtone); 1740-1735 cm^{-1} s (ester C=O); 1396 cm^{-1} m ($O\text{-}CH_2CH_2\text{-}O$ in-plane deformation); 1250 cm^{-1} sh mw, 1195 cm^{-1} m, and 1155-1148 cm^{-1} m (ester C-O-C); 1105 cm^{-1} s, 1130 cm^{-1} m, 960 cm^{-1} sh m, and 940 cm^{-1} m (acetal C-O-C).

NMR resonances ($CDCl_3$) present in DMA but absent in EA spectra were (s = singlet, m = multiplet): δ 3.30(s) for $(C\underline{H_3}O)_2CH\text{-}$; δ 3.40(m) for $\text{-}\overset{|}{C}\underline{H}\text{-}CH\begin{smallmatrix}\diagup O\text{-}\\ \diagdown O\text{-}\end{smallmatrix}$; δ 4.10 (either a broad doublet with the triacetals or a doublet of a doublet with the diacetals) for $\text{-}\overset{|}{C}H\text{-}C\underline{H}\begin{smallmatrix}\diagup O\text{-}\\ \diagdown O\text{-}\end{smallmatrix}$; 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 $\text{-}OC\underline{H}_2C\underline{H}_2O\text{-}$ and at δ 4.73 for $\text{-}\overset{|}{C}H\text{-}C\underline{H}\begin{smallmatrix}\diagup O\text{-}\\ \diagdown O\text{-}\end{smallmatrix}$ 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

TABLE II

Mechanical Properties (3,13) of Polyvinyl Chloride (PVC) Sheets Containing 32% Plasticizer

Plasticizer, 32% (sample no. from Table I)	Torsional stiffness, C		Compatibility, Δ	Tensile strength, psi	Elongation, %	100% Modulus, psi	Migration wt loss, %	Volatility wt loss, %	Heat stability (3), hr
	T_f	T_4							
Formulation I[a]									
Controls[b]:									
DOP	-25	4	29	2835	290	1165	3.0	1.5	6.5
DOS (5)	-57	-7	50	2355	295	1045	19.3	1.6	---
Plastolein 9720	-21	8	29	2830	305	1345	3.9	0.9	7.5
Dimethyl acetals:									
1B (92% Tri)	-17	10	27	2890	240	1455	1.9	0.8	4.5
2B (79% Tri)	-21	8	29	2680	235	1245	2.7	1.3	4
3B (75% Tri)	-21	8	29	2790	300	1215	2.8	1.2	4.5
4B (78% Di)	-30	4	34	2825	260	1295	6.6	3.2	4.5
5C (87% Di)	-33	6	39[c]	2495	325	1190	8.2	6.6	4
Ethylene acetals:									
6B (95% Tri)	-12	15	27[d]	2995	210	1795	1.0	1.8	4.5
7B (59% Tri)	-18	10	28	3025	320	1450	2.4	0.9	4.5
8A (84% Di)	-17	17	34[e]	3390	295	1850	2.3	2.0	3
Formulation II[f] (50:50 DOP)									
Control[b]:									
DOS/DOP (5)	-43	-5	38	2790	290	1150	12.2	1.5	7.5
Dimethyl acetals:									
>95% Mono (5)	-38	0	38	2655	350	1155	8.8	2.1	---
1B (92% Tri)	-19	5	24	2755	275	1265	2.6	1.0	4.5
2B (79% Tri)	-25	4	29	2690	310	1170	3.0	1.5	4
3B (75% Tri)	-25	4	29	2880	275	1255	2.7	1.3	4
Bu[g] (78% Tri)	-30	6	36	2645	315	1250	4.8	1.2	4
4B (78% Di)	-28	3	31	2590	210	1220	4.7	1.7	4.5
5C (87% Di)	-31	1	32	2835	310	1080	6.0	1.9	4.5
Bu[h] (91% Di)	-34	2	36	2700	330	1215	6.6	1.2	5
Ethylene acetals:									
>95% Monoacetal ester (5)	-39	1	40	2740	345	1130	8.4	2.1	---
6B (95% Tri)	-18	8	26	2885	280	1450	1.9	0.9	4.5
7B (59% Tri)	-22	6	28	2830	300	1225	2.5	1.4	4.5
8A (84% Di)	-28	4	32	2925	315	1155	4.0	1.5	4

[a] In percent by wt: Geon 101 (a commercial PVC resin), 65; plasticizer, 32; G62 (an epoxy plasticizer stabilizer), 1; Mark M (a Ba-Cd complex), 2; milling and molding as previously reported (3,12) gave 3 x 6 x 0.075 in. PVC test sheets.

[b] DOP = di-2-ethylhexyl phthalate, DOS = di-2-ethylhexyl sebacate, and Plastolein 9720 = a commercial polymeric plasticizer.

[c] Moderate exudate after 48 hr.

[d] Slight surface exudate after 2 weeks.

[e] Slight exudate after 1 week.

[f] Formulation II is the same as I except that 50% of the plasticizer is DOP.

[g] Butyl ester triacetal for comparison with methyl ester 3B.

[h] Butyl ester diacetal for comparison with methyl ester 5C.

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 (3,13).

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 $CH(OCH_3)_3$ 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 $HC(OCH_3)_3$-HCl-CH_3OH solution. An attempt was made to acetalate sample 5 in CH_3OH-$(C_2H_5)_2O$ at reflux with a strong acidic cation exchange resin by an adaptation of the method of Beal, et al. (14). However, under the conditions of this method, acetalation proved too sluggish and was driven to completion finally with $CH(OCH_3)_3$ 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 reaction conditions resulting in oxidation.

For good compatibility with PVC, plasticizers also should 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 (9), because aldehydes interfere with the standard acetic anhydride-pyridine reagent. The aldehyde esters gave reproducible, low hydroxyl values (Table I). This procedure did not work with the acetal esters,

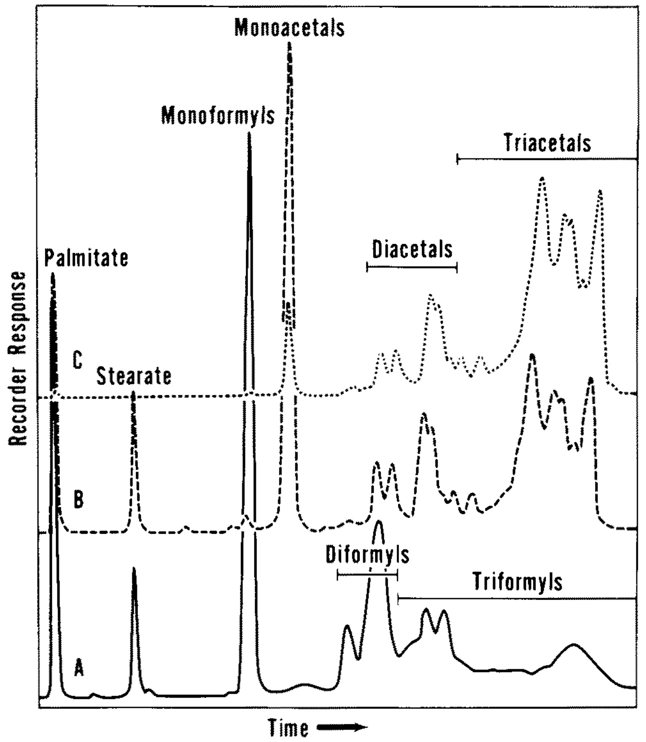

FIG. 1. Gas liquid chromatograms of hydroformylated linseed methyl esters and their dimethyl acetals. Curve A = —— hydroformylated linseed methyl esters (sample 2, Table I). Curve B = - - - - dimethyl acetals from the hydroformylated product of curve A (sample 2A, Table I). Curve C = • • • molecularly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

however. High and erratic values resulted when ethyl azelaldehydate diethyl acetal (15) was used in the PMDA procedure as a standard, even though it was free of hydroxyl groups according to GLC, TLC, and IR. Hydroxyl values determined for the various acetal esters also were not reproducible. IR spectra showed little or no hydroxyl impurity in these acetals. More hydroxyl impurity was indicated by IR 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.

With both monoformyl- and monoacetal-esters, carbonyl analyses agreed with GLC analyses. With the polyformyl- or polyacetal-esters, however, carbonyl values varied from 65-80% of the values calculated from GLC analyses. This discrepancy may be attributable to ester impurities having the same GLC retention as the acetal esters, different detector response for various components, and differential decomposition under the GLC conditions used. Carbonyl analyses also may be erroneous because optimum oximation conditions were not established for polyformyl- and polyacetal-esters. Investigation of these analytical problems was beyond the scope of this article, however.

Chromatography

Gas liquid chromatograms showing separations between palmitate and stearate, formyloleate and formylstearate, and the di- and the tri-formylstearates have been reported earlier (6). The complexity of samples in Table I is illustrated by representative chromatograms from crude, hydroformylated linseed methyl esters, their crude acetals, and distilled fractions (Fig. 1 and 2). Incomplete hydroformylation and carbon-carbon double bond hydrogenation are observed with the polyunsaturates but not with the monounsaturates (6,8), and this should be remembered when Table I is examined for the composition of aldehyde products from these hydroformylations.

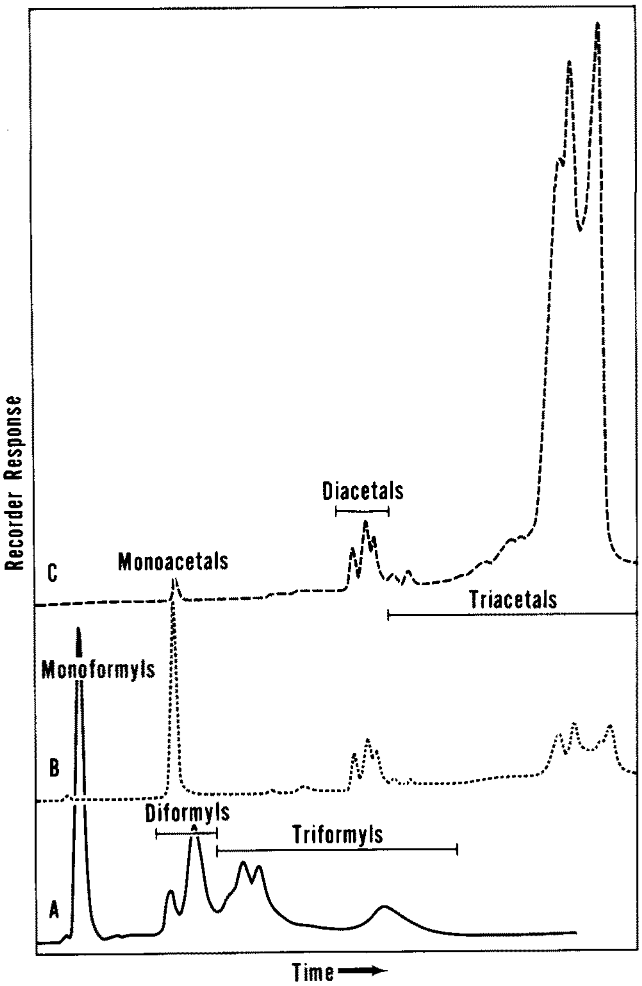

FIG. 2. Gas liquid chromatograms of hydroformylated linseed methyl esters and their ethylene acetals. Curve A = —— hydroformylated linseed methyl esters (sample 6, Table I). Curve B = • • • ethylene acetals from the hydroformylated product of curve A (sample 6A, Table I). Curve C = - - - molecularly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

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 redistillations. For example, comparison of a chromatogram of distilled sample 1B with that of crude sample 1A shows that, in sample 1B, peaks with lower retention times in either group diminished in size and area compared to the later peaks. Fractionation of isomers was not as 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 (5,12), 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 (5). Polyfunctional enol ethers were detected easily 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 detected easily 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 methyl esters show good compatibility and permanence as primary PVC plasticizers but do not improve low temperature properties. This behavior contrasts the monoacetal derivatives previously reported (5), which had less compatibility and which could be used only as secondary plasticizers. A 50:50 combination of the monoacetals with di-2-ethylhexyl phthalate (DOP) (formulation II, Table II) compared favorably with a 50:50 mixture of di-2-ethylhexyl sebacate (DOS) and DOP at a 32% plasticizer level. The diacetal samples exhibit plasticizer properties intermediate between those for the tri- and monoacetals.

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 tri-DMA ester (sample 1B, Table II) had superior migration and volatility properties. The tri-EA ester (sample 6B) had superior migration and equivalent volatility. Both the di-DMA (samples 4B, 5C) and the di-EA esters (sample 8A) had slightly higher volatility. The di-DMA ester, but not the di-EA 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.

Butyl esters were not sufficiently compatible as primary plasticizers for PVC. Using formulation II, butyl esters were less compatible (Δ36) and showed higher migration (4.8-6.6%) than the corresponding methyl esters.

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 (5,12), 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 α to the acetal group, could be an important factor in influencing heat stability. A small improvement (0.5-1.0 hr) in heat stability was obtained with the butyl esters compared to the corresponding methyl esters. More research is needed to determine if stability of these acetal plasticizers can be improved by changes in ester functionality or in formulation.

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