Alkyl Azelaaldehydates of High Purity From Alkyl Soyates: Preparation and Properties[1]

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ABSTRACT

Reductive ozonolysis of appropriate alkyl soyates in various participating media produced methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl azelaaldehydates in good yield and high purity (98+%). The participating media examined were: methyl, ethyl, *n*-propyl and *n*-butyl alcohols; mixtures of an alcohol and acetic acid; water; and mixtures of water and acetic acid. Any combination of solvent and ester, except methanol-methyl soyate, allowed good separation by fractional distillation of ester and acetal impurities from the azelaaldehydate. A preparative method was developed by which high purity ethyl azelaaldehydate is produced from soybean oil by reductive ozonolysis in water. The only major impurity by this method was ethyl hydrogen azelate, which was easily removed with a bicarbonate wash. After a single fractional distillation with a short Vigreux column, the azelaaldehydate was obtained in 78% yield and 98+% purity. Physical properties and spectral (IR, NMR and mass spectroscopy) and chromatographic data were determined for the pure alkyl azelaaldehydates. Several of these properties were also determined for acetal and diester by-products.

INTRODUCTION

Methyl azelaaldehydate has been prepared by reductive ozonolysis of methyl oleate in methanol (1) and, more recently, several reactions of this versatile, bifunctional intermediate have been reported (2). Reduction of methanolic ozonolysis products is carried out best with zinc and acetic acid. Although catalytic hydrogenation is a more economic and convenient method, it forms dimethyl azelate, a byproduct that cannot be separated from methyl azelaaldehydate or its dimethyl acetal by fractional distillation. Consequently, both yield and purity of aldehyde ester suffer. Reductive ozonolysis in a participating solvent, such as an alcohol or water, has significant advantage over that in a nonparticipating solvent. Some of these advantages include mild, convenient temperature and pressure for both ozonolysis and reduction steps, stability and freedom from chain degradation of the ozonolysis products and high yields of aldehyde products. Because of these advantages, we have continued our investigations with participating solvents and catalytic hydrogenation to improve yield and purity.

In earlier work, we used methanol (1) and certain alcohol-carboxylic acid combinations (3) with methyl oleate and water (4) with methyl soyate. We now have compared several participating media for preparation of methyl and other alkyl azelaaldehydates of high purity by reductive ozonolysis of alkyl soyates. We also obtained more consistent and more reliable physical constants for the aldehyde esters than those previously published in the literature. Three of the azelaaldehydates, the isopropyl, *n*-propyl and *n*-butyl, have not been described previously.

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EXPERIMENTAL PROCEDURES

Gas Chromatography

Gas liquid chromatographic (GLC) analyses were performed with either an F&M Model 500 or Model 810 Gas Chromatograph. A thermal conductivity detector was used with both. All columns were 4 ft X 1/4 in. aluminum. Injection port temperature was 240 C; detector block temperature, 300 C and bridge current, 150 ma (F&M 500) or 170 ma (F&M 810). Aldehyde analyses were carried out with a column of 20% SF96 on 60-80 Gas Chrom P programmed at 10 C/min (F&M 810) or 11 C/min (F&M 500) from 100 C to 290 C. Helium flow was adjusted to 50 cc/min.

Spectroscopy

IR spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. Absorption bands were determined in CCl_4 solutions. A path length of ca. 0.10 mm for the solutions was matched with that of a reference cell containing solvent. A fast scan with automatic programming of the slit width was employed. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian HA-100 using $CDCl_3$ as solvent with tetramethylsilane as internal reference. Mass spectra were determined with a Nuclide 12-90-DF mass spectrometer equipped with all glass 200 C molecular leak inlet.

Density and Refractive Index

Density measurements were made with a 5 ml, water-calibrated pycnometer of the Weld-type with a cap. Refractive index measurements were made on a Bausch & Lomb precision Abbe refractometer. Temperature was maintained at 20 C for both measurements.

Differential Thermal Analysis

Exotherms and melting point endotherms were found on a Du Pont Model 900 analyzer with silicon carbide as a reference. A micro sample was cooled with liquid nitrogen to below -60 C and then heated at 2 C/min past the melting endotherm. Crystallization exotherms were observed during the cooling process before heating. Boiling point endotherms were observed with silicone oil on glass beads as the reference. A 2-3 μl sample was injected into a micro tube containing glass beads; the sample was heated at 25 C/min under a constant flow of nitrogen (ca. 2.5 scfh). A slower heating rate caused the loss of too much sample before the boiling point was reached. Sensitivity was set at 0.2 C/in.

Alkyl Esters of Soybean Oil (Alkyl Soyates)

Soybean oil (commercial, alkali-refined and bleached) was converted readily to methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl soybean esters in 90+% yields by sodium-catalyzed alcoholysis. The reaction is illustrated in the following example for ethyl soyate. Metallic sodium (1.0 g) was added to 1100 g (23.9 moles) of dried, absolute ethanol in a 3 liter round-bottomed flask. After the reaction was complete, 845 g of oil was added. The solution was refluxed for 1 hr and then cooled. After glacial acetic acid (ca. 3 ml) was added to neutralize the catalyst, the solution was distilled to remove most of the ethanol. Upon cooling, the solution separated into two phases. The

glycerol layer weighed 84 g. The ester layer was washed with water three times and then dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 812.3 g (92.4% yield) of ethyl soyate and 36.6 g (4.3% weight) of residue. GLC indicated the following composition for the ethyl soyate: ethyl palmitate (12.2%), ethyl stearate (4.2%), ethyl oleate (25.9%), ethyl linoleate (51.5%) and ethyl linolenate (6.3%).

If further purification of soyate was desired (see Discussion), a hexane solution of the soyate (ca. 50%) was passed through a column of alumina (ca. 1:4 Al_2O_3/soyate). After the column was washed with some solvent, the effluents were combined and the solvent was removed.

Determination of Emulsion Type

Two methods were used to determine that at weight ratios of 1.4:1 or less of water to ethyl soyate, a definite water in oil emulsion exists. For the first method, a dye soluble in one phase and insoluble in another aided visual observation of the separation of phases as one phase was slowly added to the other with intermittent agitation and observation. Either 0.02% indigo carmine in water or 0.05% Oil Red O in ethyl soyate served well. In the second method, the conductivity of water and ethyl soyate mixtures was determined to confirm the type of emulsion.

Reductive Ozonolysis in Alcohols

The method is illustrated in the following example for ethyl azelaaldehydate (EAZ). A solution of ethyl soyate (100 g, 0.479 mole of unsaturation) in 225 g of *n*-propyl alcohol was ozonized at 8-10 C with a continuous stream of oxygen containing about 3% ozone (1). Ozonization was discontinued after nearly 3 hr, when ozone content of the exit gases began to increase as indicated by a Welsbach Model C ozonemeter. The solution was purged with nitrogen, and ca. 14 g of 5% $Pd/CaCO_3$ catalyst poisoned with lead acetate (5) was added. The catalyst was one that had been recovered from several previous hydrogenations. Hydrogen was introduced through a fritted glass disperser into the vigorously stirred solution at a rate of about 1.5 liter/min for 2.75 hr. A catalyst free sample of the solution failed to give a positive test for active oxygen when added to glacial acetic acid containing a few drops of 50% potassium iodide solution. After the catalyst had been removed by filtration, the filtrate was stored overnight in a freezer. (Preferably, the filtrate should be processed soon after filtration to minimize possible side reactions of malonaldehyde). The filtrate was then distilled in the presence of water to suppress acetal formation (3) and at moderate temperatures to suppress aldehyde condensations (6). To the filtrate in a 2 liter, round-bottomed flask equipped with a nitrogen capillary ebullator and a 12 in. Vigreux column was added 600 ml of distilled water. Distillation was carried out at 68-71 mm of mercury for 1.75 hr, at which point the distillate appeared turbid. During this period the vapor temperature rose from 36 to 43 C. The organic residue (96.3 g) was then distilled through a 1 X 6-in. Vigreux column maintained at 2.0-0.02 mm Hg. A fine capillary for nitrogen was used to aid ebullition. A fraction (43.3 g, 75.4% yield) was collected that boiled at 91-108 C at 0.05 mm Hg. GLC indicated a purity of 94.6% for EAZ. A higher boiling fraction, mainly palmitate and stearate, was collected for which an additional 3% yield of EAZ and a 5.3% yield of ethyl propyl azelate were indicated.

Similar preparations with other soybean esters and other solvents (3-4:1, solvent-ester ratio) were also carried out with the following results [soyate ester, solvent (mole ratio), mole % yield of RAZ, mole % yield of azelate ester, % purity of RAZ after distillation through a 1 X 6 in. Vigreux column]: Me, EtOH, 64, –, 99; Me, *n*-PrOH, 69,4.6, 95; Me, *n*-BuOH, 75, 16.8, 92; Et, EtOH, 66, 9.7, 89; Et, *n*-BuOH, 65, 6.0, 92; Pr, *n*-PrOH, 76, 4.7, 98; Bu, EtOH, 75, 5.4, 96; Et, EtOH:HOAc (5:1), 73, 8.5, 94; Pr, EtOH:HOAc (2.3:1), 70, 5.6, 92; Bu, EtOH:HOAc (5:1), 65, 10.0, 92.

Reductive Ozonolysis in Water

The method is illustrated by the following example for EAZ. Ethyl soyate (200.0 g, 0.9883 mole C=C), which had been purified with alumina (see Discussion), was added to 225 g of distilled water. The water in oil emulsion was stirred vigorously in a glass and Teflon reaction apparatus, which was immersed in a continuous flow water bath at 15-20 C. Ozonization was carried out as previously described for about 6 hr. The ozonized mixture was flushed with nitrogen and transferred with a little ether and water to a separatory funnel. This mixture was left under nitrogen at -20 C overnight.

The following morning, the mixture was thawed and most of the aqueous layer was separated at room temperature. After one quick extraction of the aqueous layer with ether, the wet organic fractions were added to 0.5 g of palladium black in either a stainless steel autoclave with magnetic agitation or a rocker shaker autoclave. The ozonolysis mixture was hydrogenated for 2.5 hr at 35-50 C with 300-400 psi of hydrogen (pressures to 800 psi have been used). The reduced mixture (negative peroxide test with acetic acid-saturated iodide solution) was filtered under nitrogen pressure and the catalyst was recovered. The filtrate was colorless and separated readily into a clear, aqueous layer and a cloudy, organic layer. The acidic, aqueous layer was separated and was extracted with a little ether. Combined organic fractions were shaken cautiously with 100 ml of 10% sodium bicarbonate, washed with water several times and then dried. Ether was removed by means of a rotary evaporator, water aspirator and water bath (below 40 C).

The crude product was fractionally distilled under partial vacuum through an insulated 0.75 X 6 in. Vigreux column. The major portion of volatile aldehydes was collected initially in a receiver in dry ice at 15 to 1 mm as the vapor temperature rose to 100 C. The residue was cooled to ca. 25 C and then pressure was reduced to ca. 0.03 mm. A major fraction, 87.3 g of EAZ distilling between 75 and 100 C/0.1-0.03 mm, was collected (yield 78%, purity 97.4%). A higher boiling fraction (48.3 g), mainly a mixture of ethyl palmitate and stearate which contained ca. 1% EAZ, was collected between 100 and 150 C/0.04 mm.

Variations in reducing conditions for similar aqueous ozonolysis products afforded the following results (catalyst or reducing agent, weight % catalyst based on soyate, mole % yield of EAZ, % purity of distilled EAZ after distillation through a 6-in. Vigreux column, weight % distillation residue): Pd black, 0.25, 77, 98, 3.2; recovered Pd black, 0.25, 78, 97, 3.0; 10% Pd/C, 0.22, 63, 95, 3.2; 10% Pd/C (63% HOAc present during ozonization and hydrogenation), 0.22, 59, 92, 5.5; 10% Pd/C (10% pyridine present during hydrogenation), 1, 77, 99, 4.9; 5% $Pd/CaCO_3$, 7, 63, 99+, 11.7; Lindlar, 10, 81, 98, 5.7; zinc and acetic acid, –, 60, 99, 15.1.

Purified Alkyl Azelaaldehydates

Methyl, ethyl, *n*-propyl and *n*-butyl azelaaldehydates were obtained via the bisulfite purification method (7) in maximum purity for characterization. Isopropyl azelaaldehydate and EAZ were also prepared in 99+% purity by redistillation (1 X 6 in. column packed with glass helices) of 97% pure fractions obtained by the ozonization in water procedure. The distillation column was heated and insu-

TABLE I

Physical Properties and Analytical Data

Ester	Purity, % by GLC	n_D^{20}	d_4^{20}	Molar refraction		Per cent carbon		Per cent hydrogen		Differential thermal analysis[a]	
				Calculated (10)	Found	Calculated	Found	Calculated	Found	T_m, C	T_b, C
Azelaaldehydates											
Methyl[b]	99+	1.4391	0.9785	50.05	50.14	64.50	64.56	9.74	9.88	-13.5	272
Ethyl[c]	98.5	1.4377	0.9595	54.66	54.76	65.98	66.48	10.05	10.02	-39.9	284
n-Propyl	98.6	1.4396	0.9501	59.28	59.41	67.25	67.49	10.35	10.38	-29.5	294
i-Propyl	99+	1.4365	0.9393	59.28	59.71	67.25	66.81	10.35	10.48	-33.3, -26.9	286
n-Butyl	99.0	1.4407	0.9413	63.90	64.01	68.40	68.20	10.59	10.78	-36.0	ca. 314
Azelaaldehydate Diethyl Acetal											
Ethyl[d]	99+	1.4320	0.9314	76.41	76.41	65.65	65.29	11.02	10.95	-33.5	309

[a] T_m is the temperature at the maximum of the melting endotherm; T_b, at maximum of the boiling endotherm.

[b] Literature data: Ref. (10) $d_4^{18.7} = 0.9938$, $n_D^{18.7} = 1.4426$, ($R_{L.L.}$ found 65.74); Ref. (11) $d_4^{20} = 0.9704$, $n_D^{20} = 1.4384$, ($R_{L.L.}$ found 50.41); Ref. (12) $d_4^{13} = 0.9542$, $n_D^{18} = 1.43705$; Ref. (13) $d_4^{20} = 0.9727$, $n_D^{30} = 1.4344$, ($R_{L.L.}$ found 49.90).

[c] Literature data: Ref. (10) $d_4^{18.5} = 0.9961$, $n_D^{18.5} = 1.4418$ ($R_{L.L.}$ found 53.18).

[d] Literature data: Ref. (14) $d_4^{19} = 0.9682$, $n_D^{19} = 1.43668$ ($R_{L.L.}$ found 98.42).

lated. The EAZ fraction boiled at 68-78 C/0.03 mm; the isopropyl azelaaldehydate fraction, at 76 C/0.03 mm.

Diethyl Acetal of EAZ

Ammonium chloride, 0.4 g, was added to a solution of triethyl orthoformate, 18.5 g (0.125 mole), and EAZ, 20.0 g (0.100 mole; 98.5% by GLC), in 10 ml of dry ethanol. This mixture was refluxed under nitrogen for 0.5 hr. Ammonium chloride was removed by filtration, and the filtrate was refiltered through a bed of sodium carbonate. Solvent was removed by flash distillation. Since GLC still showed some minor impurities, the residue was fractionally distilled to obtain a clear, colorless fraction (bp 108-111 C/0.13 mm) which weighed 23.1 g (85.6% yield). It had a purity of 99+% by GLC.

RESULTS AND DISCUSSION

Previous work has shown that the dimethyl acetal of methyl azellaldehydate can be prepared in high yields (90%) from methyl soyate (4). We now have data which show that other soyate esters can be used to prepare alkyl azelaaldehydates in good yields (70-80%) and in high purities without protection of the aldehyde group by acetal formation.

Alcoholic Media

Experimental results from reductive ozonolysis of various alkyl soyates in different alcohols or alcohol-acetic acid combinations demonstrate that any combination of solvent and ester, except methanol-methyl soyate, allows good separation by fractional distillation of diester and acetal impurities from azelaaldehydate. Acetal formation is suppressed by having water present during removal of alcohol from the ozonolysis products, and steam distillation is convenient for removing the alcohol. Lindlar catalyst is superior to Pd/C catalyst in alcoholic media since diester formation is less and yields are generally better. Yields were on the order of 65-75%, and purities varied from 90-99%. The purities are remarkable because only a Vigreux column was used and because methyl azelaaldehydate prepared by catalytic hydrogenation had been available previously only in lower purity. The alcohol-acetic acid combination in 1:1 molar ratio, so successful with methyl oleate (3), was no better than alcohol alone when applied to alkyl soyates. Molar ratios of alcohol and acid were greater than one in order to reduce the amount of alkali for neutralization. Consequently, azelate ester formation was 6-10%. This was still significantly better than the 25% azelate ester formed in the absence of acetic acid.

Aqueous Media

The effects of various reducing conditions for the aqueous ozonolysis products were evaluated. The resultant data show that if the proper hydrogenation conditions are chosen, aqueous ozonolysis products from the alkyl soyates can provide azelaaldehydate in yields comparable to or higher than those from alcoholic ozonolysis products. In addition, the crude product is easier to purify because the only major byproduct is alkyl hydrogen azelate which is easily removed with a bicarbonate wash. Yields were generally 75-80% and purities were better than 95%. Zinc and acetic acid reduction of the aqueous ozonolysis products produced a 60% yield only, in contrast to the excellent yields obtained by zinc and acetic acid reduction of alcoholic ozonolysis products.

Several attempts to hydrogenate the aqueous ozonolysis products at atmospheric pressure with palladium catalysts were unsuccessful and we subsequently found that several precautions, in addition to a moderate hydrogenation pressure, should be taken to ensure efficient, reproducible hydrogenations with palladium black. Because fractional distillation alone of the crude soyate does not achieve

TABLE II

GLC Retention Data for Azelaaldehydates, Ozonolysis Byproducts and Standards

Compound[a]	SF96 at 215 C[b] Relative retention time[c]	SF96 at 215 C[b] Equivalent chain length (17)	SF96 Programmed[b] Relative retention time[c]	DEGS at 200 C[b] Relative retention time[c]	DEGS at 200 C[b] Equivalent chain length (17)
Monoester					
Methyl C_9	0.050	8.86[d]	0.387	---	---
Methyl C_{12}	0.141	12.00	0.621	0.193	11.88[d]
Methyl C_{14}	0.274	14.00	0.760	0.329	13.86[d]
Methyl C_{16}	0.524	16.00	0.885	0.581	16.00
Methyl C_{18}	1.000[c]	18.00	1.000[c]	1.000[c]	18.00
Ethyl C_{16}	0.654	16.64	0.924	---	---
Ethyl C_{18}	1.304	18.74	1.217	---	---
Alkyl Azelaaldehydate					
MAZ	0.102	11.13	0.543	0.814	17.25
EAZ	0.128	11.73	0.600	0.871	17.50
IAZ	0.144	12.07	0.633	0.732	16.86
PAZ	0.178	12.72	0.665	1.025	18.10
BAZ	0.245	13.70	0.739	1.304	18.99
Diester					
DMAz	0.145	12.10	0.622	0.900	17.62
DEAz	0.227	13.47	0.720	0.954	17.83
Azelaaldehydate acetal					
EAZDEA	0.186	12.86	0.680	0.470	15.18
Aldehyde					
C_6	---	---	0.084	---	---
C_9	---	---	0.293	---	---

[a]AZ, azelaaldehydate; Az, azelate; A, acetal; M, methyl; E, ethyl; I, isopropyl; P, *n*-propyl; B, *n*-butyl. Example: EAZDEA is the diethyl acetal of ethyl azelaaldehydate.

[b]Data reported were determined using the F&M 810 Gas Chromatograph. Programming was from 100 to 290 C at 10 C/min (Experimental Procedures). Liquid phases: DEGS is diethylene glycol succinate and SF96 is a silicone fluid.

[c]Adjusted retention time of the standard (methyl stearate) was: 15.58 min (SF96 at 215 C); 17.48 min (SF96 programmed); 2.81 min (DEGS).

[d]See Discussion.

sufficient purity, our best results have been obtained with ethyl soyate purified on a column of alumina (distillation then is not necessary); also, an activated form of palladium black (8) can be used (Awl, Pryde and Cowan, unpublished data). Different batches of commercial catalyst have shown significant variations in activity. Consequently, initial activation of the palladium black is precautionary and reactivation after several recoveries may also be helpful.

Although the data in Table II may suggest that Lindlar or Pd/C with pyridine would be catalysts of choice, palladium black is preferred because it is readily recovered and is reusable, both crude and distilled product are colorless and a minimum of distillation residue occurs. Catalysts supported with calcium carbonate, such as Lindlar, react with acidic byproducts causing considerable loss of the catalyst. Pyridine also reacts and any pyridine that remains is difficult to remove and to recover. Although high yields (ca. 90%) of aldehyde are indicated for the crude product after a chemical reduction, the work up is hampered by persistent emulsions, isolated yields are low and considerable distillation residue is left because of condensation.

After an aqueous ozonization, the water in oil emulsion is difficult to separate into oil and water phases and it may not be convenient or practical to do so commercially. We have no evidence that such separation is necessary before hydrogenating. However, if isolation of any of the water soluble products is desired, in particular malonaldehyde, separation of the aqueous phase would probably be necessary to isolate these aldehydes as their acetals (9).

Alkyl Azelaaldehydates: Physical Properties

We have characterized the known as well as the new alkyl azelaaldehydates since published data on the methyl and ethyl esters are not in good agreement (see footnotes, Table I). The diethyl acetal of EAZ is included; the dimethyl acetal of methyl azelaaldehydate and several other azelaaldehydate acetals have previously been satisfactorily characterized (13,15). All the molar refractions determined experimentally are in close agreement with the calculated values except for the isopropyl compound which is 0.43 unit higher than calculated. Such deviation can be expected from a branched isomer (16). GLC data are reported in Table II to aid in identifying the ozonolysis products and in evaluating operational parameters. With regard to equivalent chain lengths (ECL), conditions must be adjusted according to the need for linearity at a given region of retention (17). With the conditions used for Table II one can deduce that methyl pelargonate emerges from the SF96 column soon after the air peak and is not linearly related to the logarithm of retention of the later components. Any ECL in this region will not accurately characterize the functional group unless taken from a smooth curve drawn to give methyl pelargonate an ECL of 9.00. The same argument holds true for methyl laurate and methyl myristate on the DEGS column.

IR Spectra

IR spectra determined from CCl_4 solutions of the six compounds in Table I were, in general, consistent with the

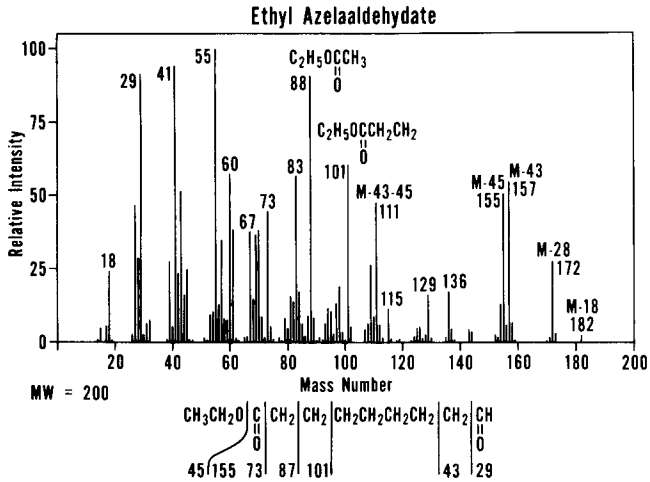

FIG. 1. Mass spectrum of ethyl azelaaldehydate.

proposed structures with one exception. Although the expected characteristic doublet (1385-1380 cm^{-1} and 1370-1365 cm^{-1}) for the isopropyl bending vibration was not apparent in our spectrum of the isopropyl azelaaldehydate, its spectrum did exhibit a strong, sharp absorption at 908 cm^{-1} which is found in the spectrum of isopropyl ether and is interpreted as isopropyl C-O-C stretching.

A weak carbonyl overtone at 3435 cm^{-1}, a medium aldehydic hydrogen stretching at 2710 cm^{-1} and variable (1045-870 cm^{-1}) and weak hydrogen deformations of the aldehyde group were observed for all the aldehyde esters but were absent in the spectrum of the acetal ester. A strong carbonyl-stretching vibration occurred at 1735 cm^{-1} in the aldehyde ester spectra and at 1740 cm^{-1} in that of acetal ester. Spectra of the aldehyde esters, but not the acetal ester exhibited weak shoulders ca. 1810-1800 cm^{-1} preceding the carbonyl-stretching absorption; the shoulder may indicate a coupled overtone. Two weak absorptions in the region of 1435 and 1415 cm^{-1} for the aldehydes and at 1445 and 1420 cm^{-1} for the acetal are ascribed to deformation of a methylene adjacent to a carbonyl group.

Several medium to strong absorptions for C-O-C stretching were observed in the 1250-1170 cm^{-1} region for all six compounds. The aldehydes showed several medium to strong C-O-C stretching bands in the 1150-1060 cm^{-1} region, whereas for the acetal these absorptions were stronger and at 1160, 1128, 1100 and 1060 cm^{-1}.

NMR Spectra

The NMR spectra of the esters share many features in common. The aldehydic proton is observed at δ 9.73 ± 0.02 and is always a triplet because of coupling with the adjacent methylene. The methylene adjacent to the aldehydic carbonyl resonates at δ 2.40 and is a doublet-split-triplet pattern. The methylene α to the carboxylic carbonyl occurs as a triplet at δ 2.26 ± 0.02. The methylene protons β to either carbonyl show overlapping resonances at δ 1.60 and the remaining methylene protons resonate at δ 1.32.

The distinguishing features of the spectra are due to the nature of the alkyl substituent. In the methyl ester spectrum a sharp singlet assigned to the carbomethoxy protons is observed at δ 3.60. A quartet and triplet pattern at δ 4.08 and 1.21 are assigned to the methylene and methyl protons, respectively, in the spectrum of the ethyl ester. The *n*-propyl ester exhibits two methylene resonances, a triplet at δ 3.98 and a multiplet at δ 1.62. The methyl triplet is found at 0.90. The *gem*-dimethyl absorption in the isopropyl derivative occurs at δ 1.20. A septet due to the remaining proton is found at δ 4.97. The *n*-butyl compound has a methylene triplet absorption at δ 4.02. There is a multiplet at δ 1.56 due to the other methylenes and a methyl triplet is observed at δ 0.90. The diethyl acetal ethyl ester exhibits a spectrum with several differences from those previously described. There is no aldehydic proton, of course, and no aldehydic carbonyl. The acetal proton absorption occurs at lowest field, δ 4.42 as a triplet, lower than that of the quartet (δ 4.08) due to the methylene of the carboethoxy portion of the molecule. The methylenes of the acetal portion give a complex absorption pattern centered at δ 3.51. The absorption of methylene α to the carbonyl is at δ 2.24; the remaining methylene absorptions occur at δ 1.56 and 1.32. The methyl absorptions overlap and are centered at δ 1.21 and 1.16.

Mass Spectra

The mass spectra of the six compounds from Table I were determined. Figure 1 shows the mass spectrum of EAZ with the principal fragmentations marked. None of the six compounds have a molecular ion peak. The spectra with the short chain alcohols, methyl and ethyl, are dominated by cleavage of the 2-3 carbon to carbon bond with rearrangement of a hydrogen to form the 74 and 88 peaks, respectively. Also noteworthy is the simple cleavage of the 3-4 carbon to carbon bond to form the 87 peak for methyl and 101 peak for the ethyl compound. All the compounds have a peak owing to loss of RO-, the alcohol moiety, to form a peak at 155 for the aldehydes and 229 for the diethyl acetal. The intensity of this peak increases with increasing chain length probably because the stabilization of energy is easier in the larger neutral fragment. All the aldehydes lose 28, probably C=O, and 43 due to cleavage β to the aldehyde carbonyl. Most of the odd-numbered mass peaks below mass 87 are hydrocarbon fragments due to multiple fragmentation of the hydrocarbon chain. The peaks usually reported for aldehydes at masses 29, $HC{=}\overset{+}{O}$ and 44, $CH_2{=}CH\overset{+}{O}H$ are not important in these compounds, probably because there are more favorable cleavages available. The diethyl acetal is dominated by cleavage to the acetal carbon to form the 103 peak $CH(OC_2H_5)_2^+$.

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