simulated hard water. Initial foam height for the 2-alkylcarboxylates in distilled water is good; however, where the alkyl groups are of comparable size rapid foam degeneration occurs in 5 min as indicated for monosodium salts (4–6). The remaining data suggest rather poor foaming properties for these salts in simulated hard water and for the sulfonated derivatives in both soft and hard water.

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Omega-Formylalkanoates by Ozonization of Unsaturated Fatty Esters[1]

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Abstract

Ozonization of the methyl esters of 11-eicosenoic, linoleic, erucic and linolenic acids gave a number of different homologous methyl ω-formylalkanoates. Complete ozonization of the monounsaturated esters formed C_{11} and C_{13} compounds with 90% conversion; partial ozonization of the polyunsaturated esters gave C_{12} and C_{15} products with maximum conversions at ca. 75% consumption of fatty ester. Thus, methyl linoleate gave 52 and 23% conversions to the 9- and 12-carbon products, and methyl linolenate gave 29, 27 and 19% conversions to the 9-, 12- and 15-carbon products. Yields of aldehyde or acetal esters in distilled products were 70–90% in preparative-scale experiments. Kinetic analysis showed that ozone attack was essentially random. Methanol was used as a participating solvent.

Introduction

RESEARCH AT THE Northern Laboratory has shown that the 9-carbon aldehyde ester, methyl azelaaldehydate, is a highly versatile chemical intermediate having a wide variety of potential applications (11–15), among them nylon-9 (8). World demand for synthetic resins, fibers and plastics has placed great value on polyfunctional materials; consequently, it seemed desirable to investigate the preparation of homologous ω-formylalkanoates as additional potential intermediates.

The formation in 55–60% yields of C_9 through C_{13} ω-formyl compounds by ozonization of unsaturated esters in glacial acetic acid has been reported (7,19). Starting materials included the methyl esters of oleic undecylenic, 11-dodecenoic, 12-tridecenoic and erucic acids, but only products from oleic, undecylenic and erucic acids were described in detail. The others were prepared as intermediates for subsequent syntheses (19). Schmidt and Grafen (16) prepared the 5- through 8- and the 12-carbon ethyl ω,ω-diethoxyalkanoates from cyclic ketones.

In the production of aldehydic compounds by reductive decomposition of ozonolysis products, the solvent has significant effect on yields. We have reported the use of methanol as a participating solvent in making methyl azelaaldehydate in more than 80% yields of isolated product (9). Extension of this study to the preparation of the C_{11} and C_{13} compounds is reported in this paper. We also describe a new technique consisting of partial ozonization to give C_{12} and C_{15} compounds as well. This technique is based on methyl linoleate and methyl linolenate, starting materials that are more readily available than the terminal olefinic esters previously used.

Experimental

Materials. Methyl oleate ($n_D^{30} = 1.4481$, I.V. = 84.3) was obtained from Applied Science Laboratories (20). Gas-liquid chromatographic (GLC) analysis did not indicate any impurities. Methyl linoleate ($n_D^{30} = 1.4574$, I.V. = 162.0) and methyl linolenate ($n_D^{30} = 1.4660$, I.V. = 241.8) were prepared from acids purified by liquid-liquid centrifugal extraction (1,2). Respective GLC analyses indicated purities of 92.6 and 88.4%. Methyl 11-eicosenoate ($n_D^{30} = 1.4505$, I.V. = 79.7) and methyl erucate ($n_D^{30} = 1.4514$) were obtained by fractional distillation through a spinning band column of the methyl esters prepared from crude erucic acid (Eastman Kodak). GLC analyses of the methyl eicosenoate indicated 95.1% of the C_{20} monoene, 1.2% of C_{18} compounds and 3.7% of C_{22} monoene. No impurities were detected for the methyl erucate fraction. New crop research has shown that *Crambe abyssinica* and mustard (5) are two seed oils rich in erucic acid. Accordingly, methyl erucate was also obtained by recrystallization of crude acids from *Crambe abyssinica* seed oil in 4:1 acetone water (4), followed by esterification and distillation. New oilseeds rich in 11-eicosenoic acid have also been reported (5).

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TABLE I

Physical Characteristics of ω-Formylalkanoates and Their Dimethyl Acetal Derivatives

Formula	Methyl ester	Physical characteristics								
		bpC/mm Hg	n_D^{30}	$d^{20}/4$	Molecular refractivity		% Carbon		% Hydrogen	
					Calc.	Found	Calc.	Found	Calc.	Found
$OCH(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3(I)$	8-Formyloctanoate	76–78/0.08	1.4344	0.9727	50.06	49.90	64.50	64.35	9.74	9.67
$(CH_3O)_2CH(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3(Ia)$	9,9-Dimethoxynonanoate	88/0.25	1.4304	0.9673	62.57	62.56	62.04	62.10	10.41	10.37
$OCH(CH_2)_9\overset{O}{\overset{\|}{C}}OCH_3(II)$	10-Formyldecanoate	94–6/0.06	1.4392	0.9595	59.30	59.23	67.24	66.96	10.35	10.22
$(CH_3O)_2CH(CH_2)_9\overset{O}{\overset{\|}{C}}OCH_3(IIa)$	11,11-Dimethoxyundecanoate	103/0.06	1.4343	0.9511	71.81	71.92	64.58	64.58	10.84	10.80
$OCH(CH_2)_{10}\overset{O}{\overset{\|}{C}}OCH_3(III)$	11-Formylundecanoate	111/0.08	1.4414	0.9518	63.92	63.89	68.38	67.87	10.59	10.60
$(CH_3O)_2CH(CH_2)_{10}\overset{O}{\overset{\|}{C}}OCH_3(IIIa)$	12,12-Dimethoxydodecanoate	102.5–03/0.02	1.4358	0.9461	76.43	76.40	65.65	65.30	11.02	10.94
$(CH_3O)_2CHCH_2CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3(IIIb)$	12,12-Dimethoxy-9-dodecenoate	112/0.03	1.4495	0.9700	75.96	75.98	66.13	66.48	10.36	10.30
$OCH(CH_2)_{11}\overset{O}{\overset{\|}{C}}OCH_3(IV)$	12-Formyldodecanoate	117–19/0.04	1.4430	0.9400	68.54	68.87	69.38	69.16	10.81	10.78
$(CH_3O)_2CH(CH_2)_{11}\overset{O}{\overset{\|}{C}}OCH_3(IVa)$	13,13-Dimethoxytridecanoate	128–29/0.05	1.4374	0.9388	81.05	81.20	66.63	66.54	11.19	11.10
$OCH(CH_2)_{13}\overset{O}{\overset{\|}{C}}OCH_3(V)$	14-Formyltetradecanoate	128/0.04[a]	1.4388^{50}	....	....	....	....		....	
$(CH_3O)_2CH(CH_2)_{13}\overset{O}{\overset{\|}{C}}OCH_3(Va)$	15,15-Dimethoxypentadecanoate	136–36.5/0.035	1.4404	0.9330	90.29	90.18	68.31	67.90	11.47	11.37

[a] Melting point 28–30C.

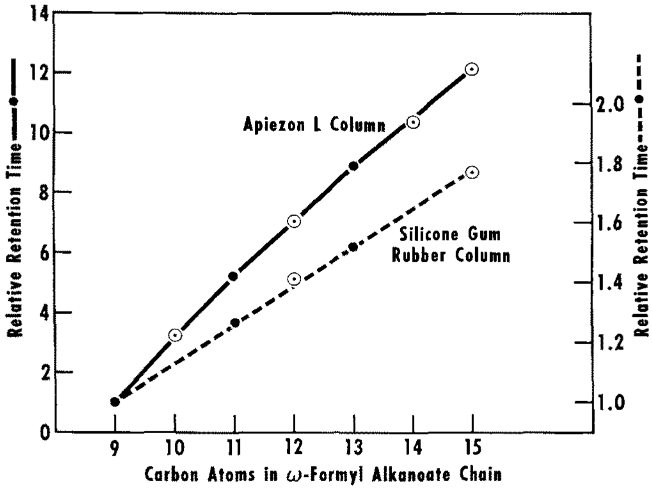

FIG. 1. Relative retention times for homologous ω-formylalkanoates in temp-programmed GLC analyses on Apiezon L and silicone gum rubber-columns. ● = standards; ⊙ = unknowns.

Gas-liquid Chromatography. Analyses were carried out on a temp-programmed chromatograph (F & M Model 500) generally at the following settings: injection port temp, 225C; block temp, 350C, rate of heating, 11C/min; programmed temp range, 100–275C; bridge current, 120 ma; helium flow, 50 ml/min. The 9-, 11- and 13-carbon ω-formylalkanoates served as standards in setting up calibration curves to identify homologous compounds on 2-ft Apiezon L and silicone gum rubber columns (Fig. 1).

Condensation and polymerization of aldehyde esters (in the column and injection port of the chromatograph) made it necessary to determine these losses for yield calculations. Therefore, a weighed amt of each aldehyde ester (9-, 11-, 12-, 13- and 15-carbon) was mixed with a weighed amt of dimethyl azelate and injected into the port under the conditions selected. Assuming no loss of dimethyl azelate, the appropriate correction factors for the aldehyde esters were determined by comparing the ratios of each with dimethyl azelate before and after GLC. These factors remained fairly constant for the conditions described; however, each had to be determined daily or whenever the conditions were changed. Typical correction factors: C_9, 1.14; C_{11}, 1.31; C_{12}, 1.38; C_{13}, 1.46; and C_{15}, 1.58 (for 2-ft, 20%-silicone rubber SE-30 column on Diatoport P, acid wahsed, 60—80 mesh).

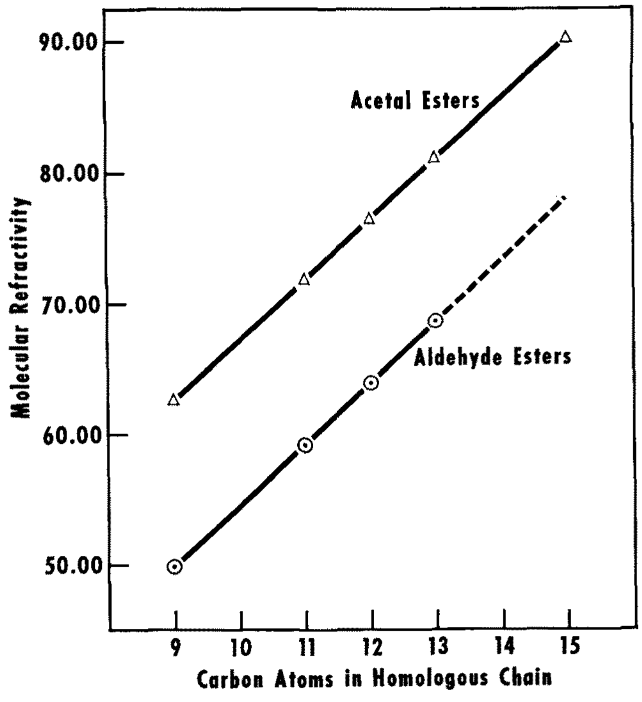

FIG. 2. Molecular refractivities of homologous ω-formylalkanoate and their dimethyl acetal derivatives.

Identification of homologous compounds was further accomplished by plotting their molecular refractivity against carbon number (Fig. 2).

Carbonyl Analyses. These were carried out by titrating the HCl liberated by the reaction with hydroxylamine hydrochloride to a standard pH (17). The carbonyl sample (2–2.5 meq) was added to 25 ml of 1*N* $H_2NOH \cdot HCl$ in 75% ethanol. To obtain complete reaction of free aldehyde and acetal the solution was refluxed 60 min if no acetal was present and 120 min if it was. Titration was carried out with 0.1*N* NaOH to the pH of a blank (usually 3.2) making use of a pH meter. Since organic acids interfere at this pH, both acids and esters (which hydrolyze in the solution) must be absent (18). The presence of nonpolar solvents as a second phase prevents completion of the oximation reaction, and such solvents must be removed before analysis.

Ozonization of Monounsaturated Fatty Esters

Methyl 8-Formyloctanoate (I). Although the preparation of I has been previously described (9), this work with larger quantities made it possible to get even better yields of isolated product. Methyl oleate (120.4 g, 0.4 mole) was ozonated in 1800 ml of methanol, and the ozonolysis products were reduced with zinc and acetic acid. After washing and recovering the aldehydes, but before isolation, the conversion of starting material to carbonyl compounds was 92% as determined by oximation analysis. Distillation was carried out through a .1 x 6-in. glass helices-packed column. Of the high-boiling materials, there were obtained a major fraction (65.3 g) boiling 94–96C/0.35 mm Hg, containing 91.7% I, and a minor fraction (4.9 g) boiling 96–120C/0.3 mm Hg, containing 74.7% I. Physical properties and elemental analyses for I and all other compounds prepared are given in Table I. A second minor fraction (3.8 g), boiling 132–147C/0.3 mm Hg and having an I.V. of 43, was a solid at room temp and presumably a mixture of methyl stearate and oleate. Because the residue was only 1.2 g, the absence of condensation or polymerization reactions was demonstrated. The total yield of product having a 90.3% purity was 96% based on the methyl oleate consumed. GLC analysis indicated the major impurity to be dimethyl acetal (Ia).

Methyl 10-Formyldecanoate (II). Methyl 11-eicosenoate (65.0 g, 0.204 mole of unsaturation) was ozonated in 325 ml of methanol at 10C, and the ozonolysis products were reduced with zinc and acetic acid. Simple distillation *in vacuo* gave a major and a minor high-boiling fraction. The major fraction (35.4 g, 87%) contained 82.8% of II, 14.7% of methyl 12-formyldodecanoate (IV), and 2.5% of the 11- and 13-carbon diesters, as indicated by GLC analysis. The minor fraction (6.67 g) consisted of 5.1% of C_{11} compounds, 33.9% of C_{13} compounds and 60.9% of starting material, corresponding to a recovery of 6.2%. The relatively high amt of 13-carbon aldehyde ester suggests the presence of some methyl 13-eicosenoate in the starting material, for which GLC analysis had indicated 95% of C_{20}. Redistillation through a 1 x 6 in. glass helices-packed column gave a fraction boiling

94–96C/0.06 mm Hg and having a purity of 96% by GLC analysis.

Methyl 12-Formyldodecanoate (IV). Ozonization of methyl erucate is described in some detail to illustrate the general procedure used for the ozonization of monounsaturated fatty esters. Methyl erucate (149.0 g, 0.420 mole of unsaturation) was dissolved in 800 ml of methanol. Oxygen containing 0.92 moles of ozone/liter was passed through the solution at 0C at a rate of ca. 2.1 liter/min for 235 min. The end point of the reaction was detected in an ozone meter (Welsbach Model C). The ozone consumed by the solution was 112% of theory, and the amt passing through the solution was ca. 1% of theory, based on unsaturation present. The solution was flushed with nitrogen, and the ozonolysis products were reduced with powdered zinc (40 g, 0.61 mole) and glacial acetic acid (48 g, 0.8 mole). An excess of zinc was used to ensure complete consumption of the acetic acid because, if remaining in excess, its removal by washing would be most difficult. During the exothermic reduction, cooling was applied to the reaction flask to maintain the temp between 20 and 25C. Solids were removed by filtration, and methylene chloride (200 ml) and water (500 ml) were added to the filtrate. The layers were separated, and the aqueous layer was extracted with five 50-ml portions of methylene chloride. The methylene chloride layers were combined and washed with water five times to ensure removal of zinc salts. The methylene chloride solution was dried over calcium sulfate and distilled on a water bath to remove any solvent. The pelargonaldehyde (50.7 g, 87.1%) was recovered by distillation without a column at 2 mm Hg with a nitrogen capillary ebullator. By GLC analysis the residue (103.0 g, 97.0%) contained pelargonaldehyde (5.9%), C_{13} aldehyde ester (93.4%) and an unknown (0.7%). A portion of this slightly colored product was distilled under vacuum using a nitrogen capillary ebullator through a 1 x 6-in. helices-packed column to obtain a water-white product. Polymeric residue from the distillation amounted to 20.6% of the product. A second fraction (63.0 g) was distilled without the helices column to give IV (52.9 g, 85.0%); GLC analysis indicated a purity of 99.1%; oximation analysis, 97.1%. Polymeric residue from this distillation amounted to 13.8% of product.

Dimethyl Acetal (DMA) Derivatives of I, II and IV. One example will represent the procedure followed in making dimethyl acetal derivatives of methyl 8-formyloctanoate (I), methyl 10-formyldecanoate (II) and methyl 11-formylundecanoate (IV).

Methyl azelaaldehydate (5.0 g, 0.027 mole, purity 99.0%) was placed in a round-bottom flask equipped with a condenser and nitrogen ebullator. Methanol (40 ml), dimethoxypropane (6 g) and 5% HCl in MeOH (1 ml) were added and refluxed four hr. Upon cooling to room temp, the solution was neutralized with dilute sodium bicarbonate, and the acetal extracted from the aqueous solution with four 25-ml portions of methylene chloride. The extracts were combined, backwashed three times with water (until neutral to alk-acid paper), dried and filtered; the solvent was removed on a rotary evaporator. With distilled petroleum ether as a carrier, the residue was then passed through a 3-in. column packed with activated alumina and charcoal (9:1). After the pentane-hexane was removed on a rotary evaporator, a water-white liquid, Ia (6.05 g, 97% yield) was obtained. GLC analysis indicated a purity of 99.1%.

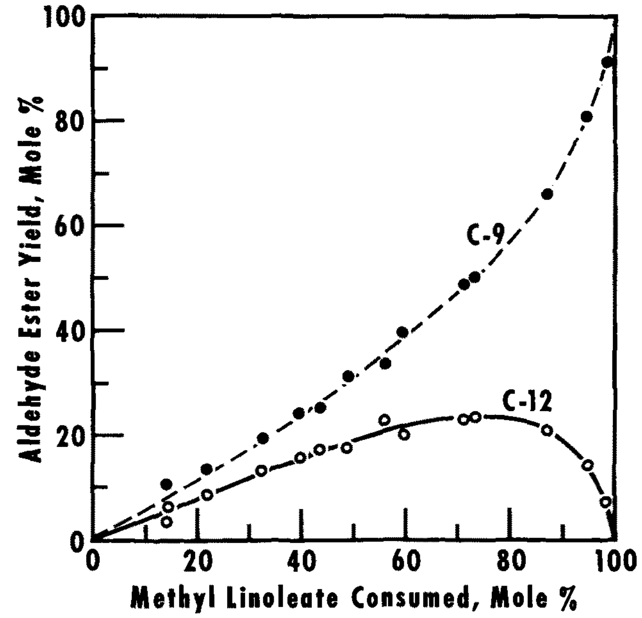

FIG. 3. Conversion of methyl linoleate to methyl 8-formyloctanoate (C_9) and methyl 11-formyl-9-undecenoate (C_{12}).

Compound II (7.6 g, 0.0355 mole, purity 91.0%) was treated in the same manner as I, giving IIa (8.81 g, yield 95%) having a GLC purity of 92.0%. Similarly, IV (6.8 g, 0.028 mole, purity 99.1%) was treated like I and II, giving IVa (7.8 g, yield 96.5%).

Activated alumina was used to remove all traces of acid catalyst. The activated charcoal removed traces of color resulting from the acetal preparation.

Partial Ozonization

Kinetic Studies on Methyl Linoleate. Methyl linoleate (10.0 g, 0.066 mole unsaturation) in 200 ml of methanol was ozonated in stepwise fashion at 0C. Samples (5 ml) were withdrawn after each 5–15%

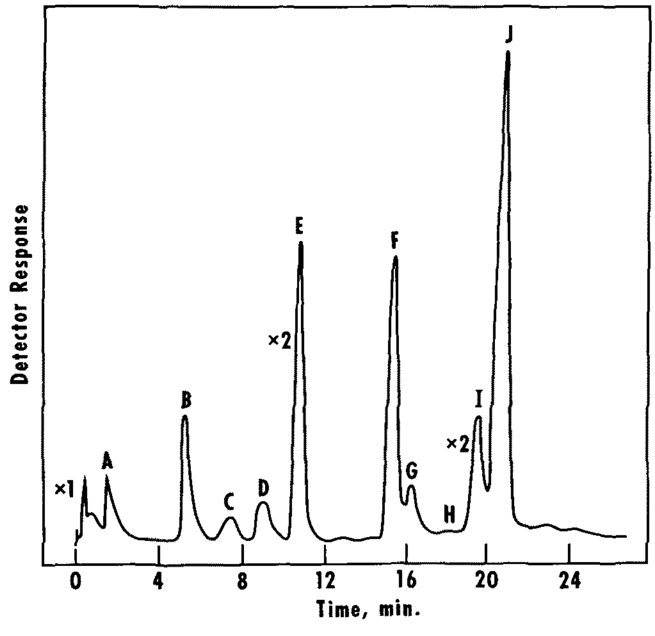

FIG. 4. Typical temp-programmed chromatogram of partially ozonized methyl linolenate. Peak A (112C), caproaldehyde; B (142C), pelargonaldehyde; C (160C), unknown; D (173C), unknown; E (185C) methyl 8-formyloctanoate (C_9); F (220C), methyl 11-formylundecanoate; G (227C), unknown; H (243C), methyl palmitate; I (254C), methyl 14-formyltetradecanoate (C_{15}); and J (264C), methyl linolenate.

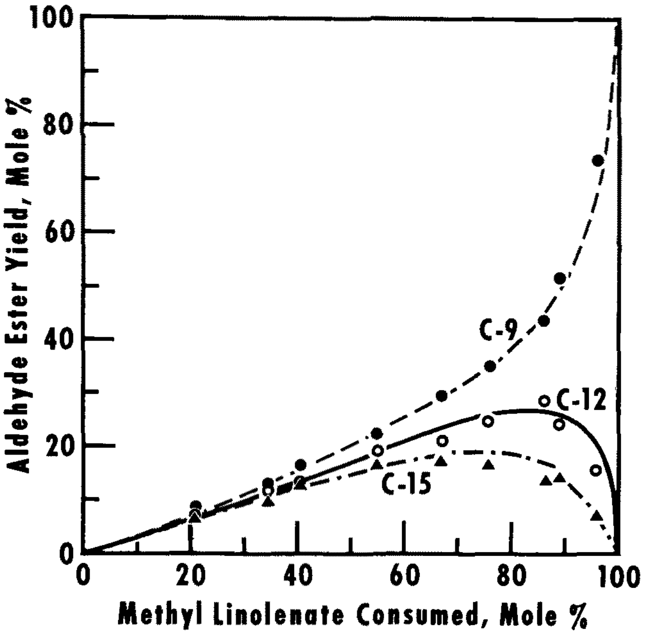

FIG. 5. Conversion of methyl linolenate to methyl 8-formyloctanoate (C_9), methyl 11-formyl-9-undecenoate (C_{12}) and methyl 14-formyl-9,12-tetradecadienoate (C_{15}).

portion of ozone added. Each sample was treated with zinc and acetic acid, filtered, dissolved in methylene chloride and washed with water until neutral. GLC analysis was run on each sample, and amt were calculated in terms of mole percentage conversion of the C_9 and C_{12} aldehyde esters fromed and of the methyl linoleate consumed (Fig. 3).

Kinetic Studies on Methyl Linolenate. Methyl linolenate (10.0 g, 0.098 mole unsaturation) in 110 ml methanol was ozonated in stepwise fashion, and samples were withdrawn and treated as before. GLC analysis could not be made directly because of polymerization of the doubly unsaturated C_{15} aldehyde ester on the chromatographic column. Accordingly, each sample was hydrogenated with a palladium-on-charcoal (Pd/C) catalyst in methanol solution at room temp and atmospheric pressure. Under such conditions, saturation of the olefinic bonds occurs with no loss of carbonyl. Catalytic hydrogenation was not carried out on the ozonolysis products since this method of reduction results in the formation of by-product methyl esters (9). GLC analysis was then made on the hydrogenated aldehyde esters with results typified in Figure 4. The amt in mole percentage of the C_9, C_{12} and C_{15} aldehyde esters were then plotted against methyl linolenate consumed (Fig. 5).

TABLE II

Preparation of Methyl 12,12-Dimethoxydodecanoate (IIIa) and Methyl 15,15-Dimethoxypentadecanoate (Va) by Partial Ozonization of Methyl Linolenate

Component	Product composition		Conversion (Yield[b]), %		
	Wt %	Mole[a] %	Before distillation	After distillation	After recrystallization
Caproaldehyde dimethylacetal	14.0	.....	....	....	....
Pelargonaldehyde dimethylacetal....	7.3	......	....	....	....
Methyl 9,9-dimethoxy-nonanoate (Ia)	35.1	50.8	37.2(40)	39.3(43)	....
Dimethyl 1,9-nonanedioate......	0.4	0.6	....	....	....
Methyl 12,12-dimethoxy-dodecanoate (IIIa)...............	19.0	23.4	17.2(19)	15.6(17)	9.7(11)
Dimethyl 1,12-dodecanedioate ..	0.6	0.8	....	....	....
Unknown	0.2	......	....	....	....
Methyl palmitate	1.0	.....	....	....	....
Methyl 15,15-dimethoxy-pentadecanoate (Va)	12.9	13.6	10.6(12)	5.9(6)	4.4(5)
Methyl stearate....	9.5	10.8			....
Total	100.0	100.0	65.0(71)	60.8(66)	

[a] Calculated on the basis of the carboxyl-containing fragments of the cleaved methyl linolenate.

[b] Calculated on the basis that the methyl linolenate not ozonized is recoverable and could be recycled.

Dimethyl Acetal Derivatives of III and V. Methyl linolenate (200 g, 1.904 mole unsaturation) was ozonized in 600 ml methanol and 82 g pyridine to 75.2% of theory. [We have previously described the usefulness of pyridine-methanol as an ozonolysis medium (10). However, no advantage over methanol alone was demonstrated in this experiment.] The peroxidic material was chemically reduced with zinc dust and acetic acid at a maximum temp of 15C. After the solution was filtered to remove zinc salts, 500 ml of water was added to the filtrate in a separatory funnel. The aqueous solution was extracted five times with 60-ml portions of ether, and the extracts were combined, washed three times with dilute HCl to remove traces of pyridine, and then three times with water (until neutral to alk-acid test paper). The ether was removed on a rotary evaporator and 1000 ml methanol and 0.2 g Pd/C were added to the residue and hydrogenated overnight. After the catalyst was removed by filtration, the dimethyl acetal derivatives were formed by refluxing the filtrate in the presence of 200 ml dimethoxy propane and 0.1 g $KHSO_4$ for four hr. The acetals were extracted from an aqueous solution of the refluxed filtrate and washed until neutral. The solvent was removed from a small portion of the neutral solution and analyzed by GLC (composition given in Table II). Upon cooling the solution to 0C, 7.0 g of methyl stearate was precipitated and removed. The solvent was removed on a rotary evaporator and the residue (158.5 g) was distilled through a 1 x 6-in. helices-packed column with the following main fractions: a) 62.89 g, bp 80–82C/0.05 mm Hg, $n_D^{30} = 1.4304$; purity, 93.6 Ia; b) 24.10 g, bp 105–107C/0.04 mm Hg, $n_D^{30} = 1.4388$; purity, 88.6 IIIa; c) 37.4 g, mixture C_{12} DMA ester (16.3%), C_{15} DMA ester (30.0%), and methyl stearate (50.0%), bp 112–70C/0.04 mm Hg; residue 13.0 g.

Because acetals have a tendency to split off alcohol at distillation temp, fractions b and c were each placed in solutions of 100 ml methanol containing 1–2% HCl and allowed to stand overnight. Water was added to the methanol solutions and the acetals were extracted with CH_2Cl_2; after extraction, the fractions were washed until neutral; and the solvent was removed on a rotary evaporator. Fraction b $n_D^{30} = 1.4365$ was recrystallized three times from a 5% solution in methanol at −40C (GLC purity 97.9%) then three times from redistilled pentane-hexane at −40 to −45C. GLC purity, 100% IIIa; oximation analyses, 98.7%; recovery of acetal 17.1 g (80%).

Fraction c was recrystallized five times from a 5% solution in pentane-hexane at −30 to −35C. GLC purity, 94.6% Va; chemical purity, 94.1%; yield, 8.81 g; recovery of acetal, 79%.

Table II gives the yields of IIIa and Va and the various acetal derivatives.

Methyl 11-Formylundecanoate (III). Methyl linoleate, 200 g in 700 ml of methanol, was ozonized to 57% of theory. Reduction of peroxidic material was accomplished by use of 0.8 mole zinc dust and 1.5 mole acetic acid (maximum temp, 25C). The excess zinc was removed by filtration and the filtrate extracted with three 100-ml portions of methylene chloride. The extracts were combined and washed with H_2O until neutral. After drying the neutral solution, the methylene chloride was removed on a rotary evaporator and 0.2 g Pd/C and 500 ml methanol were added to the residue. Hydrogen was passed through the solution while stirring until no more uptake occurred with small aliquots placed in a microhydrogenator. The mixture was filtered, and methanol removed on a rotary evaporator. The residue amounted to 210 g. Table III gives the composition of the residue.

The residue was distilled and the following fractions were obtained: a) bp 30–89C/0.4 mm Hg, 52.0 g; b) bp 89–94C/9.4 mm Hg, 1.0 g; c) bp 94–97C/0.4 mm Hg, 69.1 g; purity, 91.4% I; d) bp 97–99C/0.4 mm Hg, 5.3 g; purity 53.0% I; e) bp 111–113C/0.08 mm Hg, 32.6 g; purity 93.0% III; f) bp 113–125C/0.08 mm Hg, 6.2 g; purity 13.0% III; g) bp 130C/0.08, 31.0 g methyl stearate. Residue, 12.6 g. Solid carbon dioxide trap, 8.0 g. Distillation time, three hr and 30 min. See Table III for yields.

Fraction e was recrystallized four times from a 5% solution of petroleum ether at −40 to −45C. Recovery, 27.6 g or 85% GLC purity, 99.7%; chemical purity, 99.1%.

Methyl 14-Formyltetradecanoate (V). Efforts to isolate V from the ozonization of methyl linolenate treated in the same manner as III were not successful. The aldehyde ester could not be fractionated, and it condensed readily at distillation temp. Likewise, attempts to purify V by low-temp crystallization were unsuccessful (only ca. 1.0 g, having a GLC purity of 94.6%, mp 28–30C and $n_D^{50} = 1.4388$, was isolated). The boiling point, 128C/0.04 mm Hg, was determined by use of a percolator boiling-point apparatus.

Methyl 12,12-Dimethoxy-9-Dodecenoate (IIIb). Methyl linoleate (200 g, 1.28 mole unsaturation) in 500 g methanol and 50 ml pyridine was ozonized (at 10–14C) to 48% of theory (based on unsaturation consumed). The ozonolysis solution was reduced chemically with 50 ml glacial acetic acid and 25 g zinc dust at temp not exceeding 25C, filtered and scrubbed with dilute HCl until slightly acid. The aqueous solution was then extracted with five 100-ml portions of CH_2Cl_2, and the extracts were combined and backwashed with water until neutral. This netural material was dried and filtered, and the solvent removed on a rotary evaporator. To the residue was added 800 ml CH_3OH, 200 ml dimethoxypropane, and 10 ml of 5% HCl in MeOH. The mixture was refluxed for four hr, cooled to room temp, neutralized with dilute $NaHCO_3$ and extracted five times with 100-ml portions of CH_2Cl_2. The extracts were combined, washed twice with H_2O, dried and filtered, and the solvent was removed. The residue (207.8 g) was analyzed by GLC (Table IV).

Flash distillation of the residue at 0.06 mm Hg gave a low-boiling fraction (below 100C, 46.6 g) and a high-boiling fraction (145.7 g); also, a residue of 15.5 g. The high-boiling material was distilled through a spinning band column and the following main fractions were taken a) 46.8 g, bp 113C/4 mm Hg; GLC purity, 92.3% Ia; b) 17.35 g, bp 135–39C/4 mm Hg, GLC purity, 94.4% IIIb; c) 16.8 g, bp 140–50C/4 mm Hg; GLC purity, 52.6% IIIb, and 47.4% methyl ester; residue 63.8 g (primarily methyl linoleate).

Fraction b was recrystallized at −30C from a 5% solution in methanol. Recovery of IIIb, 98% or 17.0 g; purity 96.6%.

TABLE III

Preparation of Methyl 11-formylundecanoate (III) by Partial Ozonization of Methyl Linoleate

Component	Product composition		Conversion (yield[b]), %		
	Wt %	Mole %[a]	Before distillation	After distillation	After recrystallization
Caproaldehyde	19.5	......	......	......	......
Pelargonaldehyde	12.5	......	......	......	......
Methyl 8-formyloctanoate (I)	34.1	60.0	56.6(70)	52.2(64)	......
Methyl 11-formylundecanoate (III)	14.2	20.4	19.3(24)	19.6(24)	17.8(22)
Methyl palmitate	1.8		......	......	......
Methyl stearate	17.9	19.6	......	......	......
Total	100.0	100.0	75.9(94)	71.8(88)	......

[a] Calculated on the basis of the carboxyl-containing fragments of the cleaved methyl linoleate.
[b] Calculated on the basis that methyl linoleate not ozonized is recoverable and could be recycled.

Fraction c was hydrogenated in the presence of Pd/C catalyst then recrystallized twice from ethanol at −20. Recovery of C_{12} as III, 6.0 g; purity 85.9%; (Table IV).

Discussion

Ozonization of Monoethenoid Fatty Esters. Prior results have shown that when methanol is used as a participating solvent for the ozonization of methyl oleate and when the resulting alkoxyhydroperoxides are subjected to chemical reduction (by zinc powder and acetic acid), pelargonaldehyde and methyl azelaaldehydate are obtained with minimum side reactions (9). Consequently, methanol was used as a participating solvent with each of the starting esters, methyl oleate, methyl 11-eiconsenoate and methyl erucate, to obtain ω-formyl esters (I, II, IV in Table I) and pelargonaldehyde. However, our ozonolysis results indicated the presence of methyl 13-eicosenoate in the 20-carbon fatty acid methyl ester, so that some heptaldehyde and methyl 13-formyltridecanoate were also produced.

Yields of C_9, C_{11}, C_{13} aldehyde esters in distilled products were 87, 77 and 86%, respectively. (The relatively low yield for the C_{11} aldehyde ester does not include the methyl 13-formyltridecanoate also formed in 17% yield. The total yield of aldehyde esters from the C_{20} monounsaturated ester was 94%.)

Isolation of these aldehyde esters and their dimethyl acetal derivatives by fractional distillation should be carried out quickly in the absence of acidic and basic

TABLE IV

Preparation of Methyl 12,12-Dimethoxy-9-Dodecenoate (IIIb) by Partial Ozonization of Methyl Linoleate

Component	Product composition		Conversion (yield[b]), %		
	Wt %	Mole %[a]	Before distillation	After distillation	After recrystallization
Caproaldehyde dimethylacetal	13.9	......	......	......	......
Pelargonaldehyde dimethylacetal	10.3	......	......	......	......
Methyl 9,9-dimethoxynonanoate (Ia)	21.8	34.4	28.7(46)	27.4(44)	......
Dimethyl 1,9-nonanedioate	1.3	......	......	......	......
Methyl 12,12-dimethoxy-9-dodecenoate (IIIb)	14.8	19.9	16.7(27)	13.6(22)	11.7(19)
Methyl palmitate	1.0	......	......	......	......
Methyl linoleate	36.9	45.7	......		......
Total	100.0	100.0	45.4(73)	41.0(66)	

[a] Calculated on the basis of the carboxyl-containing fragments of the cleaved methyl linoleate.
[b] Calculated on the basis that methyl linoleate not ozonized could be recycled.

TABLE V
Partial Ozonization of Polyunsaturated Fatty Esters

Compound	Products from	
	Methyl linoleate	Methyl linolenate
Aldehyde ester	C_9, C_{12}	C_9, C_{12}, C_{15}
Monoaldehyde	C_9, C_6	C_9, C_6, C_3
Dialdehyde	C_3	C_3

catalytic substances at as low a temp as possible to avoid condensation and polymerization reactions. Prolonged heating and pot temp in excess of 150C were avoided because the amt of residual material left after distillation increased with the length of the carbon chain and distillation time. These two-component mixtures were separated in excellent yields because the wide difference in boiling range between pelargonaldehyde and the ω-formyl esters allowed for rapid distillation in simple apparatus.

Partial Ozonization of Polyethenoid Fatty Acid Esters. Relatively pure methyl linoleate and methyl linolenate were prepared from the unsaturated acids isolated from soybean and linseed acids by liquid-liquid centrifugal extractions (1,2). The various products expected from the partial ozonization of linoleate and linolenate may be seen in Table V. No attempt was made to isolate quantitatively the low-boiling and water-soluble aldehydes. When methanol was used as the solvent media for the ozonization of polyunsaturates and when their ozonolysis products were chemically reduced, the following conversions were obtained in kinetic studies: 23 mole per cent of C_{12} aldehyde ester from methyl linoleate; 27 mole per cent 12-carbon and 19 mole percent of 15-carbon aldehyde esters from methyl linolenate. In preparative-scale experiments with 200-g quantities, the conversions (yields) of aldehyde or acetal esters obtained are given in Tables III, IV and V. The calculations for yields were made on the assumption that unozonized unsaturated fatty ester could be recovered and recycled before a hydrogenation step. Although unreacted starting material was converted to methyl stearate in exploratory experiments, still recycling should be feasible on an industrial scale. A few preliminary experiments indicated that liquid-liquid centrifugal extraction may be suitable for isolating starting material from the complex reaction product. Such a procedure would eliminate isolation by fractional distillation.

Theoretical yields of C_{12} and C_{15} aldehyde esters may be made higher than those indicated (e.g. to a maximum of ca. 50% yield of the C_{12} aldehyde ester) by stopping the reaction at an earlier point, if low conversions are feasible. Low conversions would require isolation and recycling of large quantities of starting material relative to the reaction products desired.

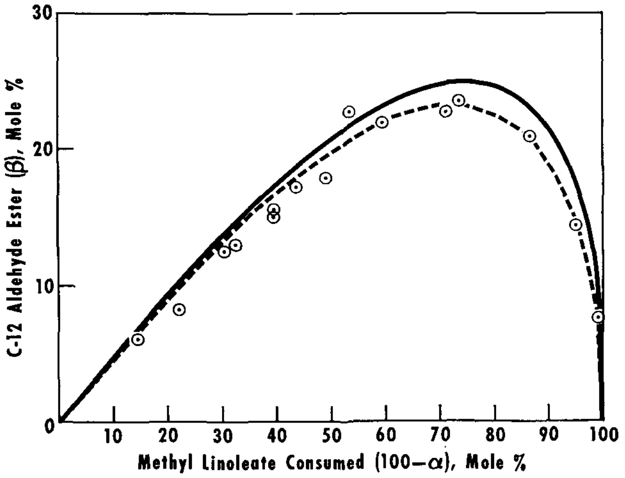

FIG. 6. Theoretical curves for conversion of methyl linoleate to C_{12} aldehyde ester when k = 1 (solid line) and K = 1.2 (dotted line).

The isolated yield of aldehydic products was lower than theoretical for the following reasons: a) Chemical reduction (by zinc powder and acetic acid) of the complex mixtures of partially ozonized polyunsaturated olefins does not proceed as smoothly as the chemical reduction of ozonolysis products of monounsaturated olefins. The instability of the unsaturated aldehydes, especially in acidic media, results in their partial polymerization and condensation when reduction, extraction and washing are not carried out below 20C (best results were at 0–5C). b) Distillation of the multi-component mixtures from polyolefin ozonizations is not as simple as isolation of products from monounsaturated ozonizations. These multi-component mixtures require more time and elaborate distillation apparatus to isolate the end products (resulting in large product losses due to polymerization and condensation). The losses may be kept to a minimum by distilling the aldehydic materials as their dimethyl acetal derivatives. The main difficulty with these simple acetals is their tendency to split off alcohol at distillation temp; nevertheless, the alcohol can easily be added back to the resulting enol ether by letting the material stand in the presence of 1% HCl in the required alcohol for four hr. The exceptionally stable ethylene glycol acetals, which do not crack at distillation temp, may also be used (14). The 15-carbon compounds could not be separated readily from the unreacted starting material by our distillation techniques.

The formyl esters having residual unsaturation were unstable and could not be distilled. Even as the acetal derivative the C_{15} unsaturated compound could not be distilled without formation of large amt of residue.

Kinetics. The treatment of the kinetics of the ozonization of methyl linoleate follows closely the methods discussed by Frost and Pearson (3). If the cleavage rates of both double bonds in methyl linoleate are considered to be the same (rate constant k_1), and the cleavage rates of the double bonds in the unsaturated aldehyde fragments are assumed to be the same (rate constant k_2), then K may be expressed as the ratio $\frac{k_2}{k_1}$.

Even though experimental data for the conversion of methyl linoleate to C_{12} aldehyde ester does not fit the theoretical curve $K = 1$ (see Fig. 6), the value for K does approximate $K = 1.2$, which is close enough to assume for all practical purposes that ozone cleavage of the double bonds is random.

When $K = 1$, the maximum conversion to C_{12} aldehyde ester is 25% (yield 33%), at the point where 75% of the methyl linoleate is consumed; however, if the reaction is run at low conversion with recycling, the yield of C_{12} aldehyde ester could be raised theoretically to 50%.

Purification by Low-Temperature Fractional Crystallization. The instability of the aldehydic materials when isolated by distillation prompted us to explore low-temp crystalliaztion as a method of purification. Compounds I and III, containing no more than 25% impurity (of dimethyl acetal or mono- and di-esters), were successfully recrystallized from 5% solutions in petroleum ether in 80–85% recovery of products having purities of 99%+. However, only a small amt of V could be isolated from this solvent mixture. When this solvent system was applied to the recrystallization of the acetal derivatives, Ia, IIIa and Va were successfully isolated from products containing up to 50% impurity (of aldehyde, mono- and di-esters) in the order of 80% recovery of 95–100% purity. Larger amt of impurity could be tolerated because the lower crystallization temp of the acetals allowed removal of most of the impurities crystallizing at higher temp. The products obtained by this crystallization procedure could be distilled rapidly without careful fractionation.

Partial ozonization of polyunsaturated fatty acids or esters followed by oxidative decomposition of the ozonolysis products is being studied further.

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Alkaline Isomerization of Methyl Crepenynate[1]

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Abstract

Methyl crepenynate (methyl-*cis*-9-octadecen-12-ynoate) is readily isomerized by potassium hydroxide in ethylene glycol to an 8,10,12-octadecatrienoic acid in good yield. A reaction carried out at 120C for 1 hr in 10% base is sufficient to convert the nonconjugated enyne system completely to conjugated triene systems.

Introduction

An earlier report from this laboratory (11) described the isolation and characterization of crepenynic (*cis*-9-octadecen-12-ynoic) acid from seed oil of *Crepis foetida* L. Preliminary data showed that crepenynic acid formed conjugated triene on heating with alkali (11) according to the AOCS method for determining polyunsaturated acids (1) in vegetable oils. These data also indicated that the reaction with crepenynic acid is more rapid and results in a greater yield of conjugated triene than does the comparable alkaline isomerization of linolenic acid.

The rearrangement of simple acetylenes to allenes and isomeric acetylenes by treatment with base has been well established by many workers. They have shown that conjugated enynes (8,10), conjugated diynes (3,7) and nonconjugated diynes (6,15) also undergo rearrangement reactions when treated with base. One of the conjugated enynes, ximenynic (*trans*-11-octadecen-9-ynoic) acid, forms conjugated trienes (8).

The object of this study is to present detailed information on the reaction of crepenynic acid with alkali under variations in time, temp, base concn and sample size. Since crepenynic acid represents a new type of naturally occurring acetylenic fatty acid, it is desirable to identify the alkali-isomerization products. Therefore, results of some experiments designed to characterize these rearrangement products are given here.

Experimental

Preparation of Methyl Crepenynate. Pure methyl crepenynate was obtained by countercurrent distribution of the mixed methyl esters of *Crepis foetida* L. seed oil as described previously (11).

Infrared Analyses. The IR spectra were determined on carbon disulfide solutions of the methyl esters in a 1-mm sodium chloride cell with a Perkin-Elmer Model 137-0001 spectrophotometer.

Alkali Treatment of Methyl Crepenynate. The potassium hydroxide-ethylene glycol solutions were prepared and standardized according to the AOCS method for polyunsaturated acids. The base solution (25.0 ml) was placed in a 50-ml round-bottom flask fitted with a small cold-finger condenser inside a larger air condenser. Nitrogen was admitted through a bubbler, placed so that the tip was well immersed in the solution. Two such apparatus (one for a blank) were then heated in an oil bath at the desired temp and allowed to remain in the bath for 15 min. The sample of ester was then introduced in a glass cup, and the contents of the flask were swirled periodically during the first few min. At predetermined intervals, 1.0-ml aliquots of sample and blank were removed, diluted immediately with absolute ethanol, and analyzed promptly on a Beckman DU spectrophotometer for conjugated triene content (1). No corrections for expansion of the ethylene glycol solutions were made in the calculations.

The preparative-scale isomerization (1.0 g) was carried out in the same manner except that a 500-ml flask containing 200 ml of 10% potassium hydroxide in ethylene glycol at 121C was used.

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