The Preparation of Polyunsaturated Aliphatic Aldehydes *via* the Acyloin Condensation[1]

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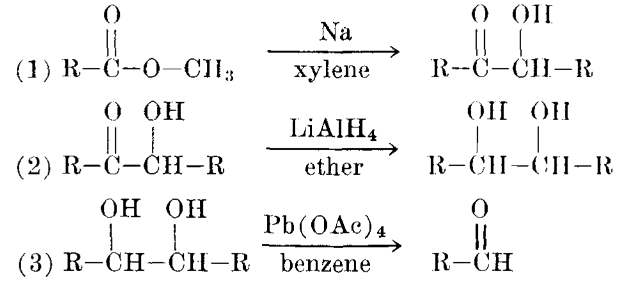
Olealdehyde, linolealdehyde, and linolenaldehyde have been recently prepared by Mangold, using a modified Grundmann reaction (1). At about the same time Kaufmann and Kirschnek prepared the two latter compounds by a similar technique (2). Bouquot and Paquot have synthesized the oleyl and erucyl derivatives by cleavage of the glycols derived from the corresponding acyloins (3). The use of the acyloin intermediate however has not been extended to the preparation of long-chain polyunsaturated aldehydes. This approach seemed to merit consideration as a means of obtaining these compounds since the yields are high and little destruction of the unsaturation would be anticipated. Furthermore the reduction of the acyloins and subsequent cleavage of the glycols may be effected quantitatively and under mild conditions.

The present contribution is concerned with the preparation, *via* the acyloin condensation, of aldehydes from methyl linolenate and from a fraction of highly unsaturated methyl esters derived from menhaden oil.

Experimental

The following sequence of reactions represents the synthesis:



$$(1)\ R-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow[\text{xylene}]{Na} R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-R$$

$$(2)\ R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-R \xrightarrow[\text{ether}]{LiAlH_4} R-\overset{OH}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H}-R$$

$$(3)\ R-\overset{OH}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H}-R \xrightarrow[\text{benzene}]{Pb(OAc)_4} R-\overset{O}{\overset{\|}{C}H}$$

The intermediate and final products were analyzed by standard methods and by the relatively new technique of thin-layer silicic acid chromatography.

Materials and Equipment

Pure methyl linolenate was purchased from the Hormel Foundation, Austin, Minn. (I.V. 272.5, 0.49% conjugated diene, no conjugated triene). Methyl esters were prepared from menhaden oil by transesterification, and a highly unsaturated fraction, free of unsaponifiable matter, was obtained by molecular distillation (I.V. 252.2, sap. eq. 315.8, trace of conjugated diene).

As in previous work (4,5,6), thin layers (250 to to 275 μ) of silicic acid on glass plates (20 x 20 cm.) were prepared by the method of Stahl (7). The apparatus for the application of the silicic acid films was obtained from C. Desaga, G.m.b.H., Heidelberg, Germany, together with "Silica Gel G," which is produced by E. Merck A.G., Darmstadt, Germany.

Preparation of Glycols

Hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol. The acyloin condensation was carried out, using methyl linolenate according to the method of Hansley (8). Into a reaction flask equipped with mechanical stirrer, dropping funnel, condenser, and gas-bubbling tube were placed 100 ml. of freshly distilled xylene and 1.6 g. (0.070 mole) of sodium. The temperature was raised to 115°C., and a fine dispersion of sodium was formed by vigorous stirring of the mixture. After the suspension had been bubbled with 99.99% nitrogen for about 15 min., 10.0 g. (0.034 mole) of methyl linolenate were added over a period of 30 min. The reaction was continued for an additional 30 min. after addition of the ester was complete. It is essential that the mixture be continuously bubbled with pure, dry nitrogen. The reaction mixture was allowed to cool to approximately 85°C., then a slight excess of methanol was added to destroy the residual sodium. This step was immediately followed by the addition of 100 ml. of distilled water, and the mixture was transferred to a separatory funnel and allowed to cool to room temperature. Ethyl ether (100 ml.) was added, and the aqueous phase was removed. The organic layer was washed with water until free of soaps, then once with dilute hydrochloric acid, and finally with water until the washings were neutral. The organic phase was dried over anhydrous sodium sulfate and filtered, and the solvent was removed on a rotary evaporator. A yield of 8.6 g. of crude linolenoin was obtained.

A solution of the crude linolenoin in ethyl ether was added over a period of 15 min. to a flask containing 0.83 g. (0.022 mole) of lithium aluminum hydride in 100 ml. of anhydrous ethyl ether. The reaction mixture was refluxed for 1 hr. and then worked up in the usual manner. The crude glycol in petroleum ether (b.p. 30–60°C.) was placed on a 200-g. column of 1:1 silicic acid (Mallinkrodt, chromatographic grade) and cellulose powder (Whatman, coarse grade) previously saturated with petroleum ether. Elution with 90:10 petroleum ether-ethyl ether gave 7.9 g. of the pure glycol (m.p. 46–48°C.). The product was a white wax-like solid that was difficult to crystallize. The over-all yield of hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol was 88%, based on the starting ester.

Analyses: Vicinal glycol by periodate: 99.2%. Calculated for $C_{36}H_{62}O_2$: C, 82.06; H, 11.86. Found: C, 82.80; H, 11.94.

Glycols from Menhaden Oil. When 10.0 g. (0.032 mole) of esters derived from menhaden oil were used as starting material, an over-all yield of 8.1 g. (89%) of pure mixed glycols was obtained.

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Analyses: Vicinal glycol by periodate: 99.6%. Iodine value found: 272.7. Theoretical: 277.7.

Preparation of Aldehydes

Linolenaldehyde. About 7.5 g. (0.017 mole) of lead tetraacetate and 25 ml. of benzene containing 5.0 g. (0.0087 mole) of hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol were heated to 60°C. for 3 hrs. After the excess reagent was destroyed with ethylene glycol, the solution was poured into 125 ml. of 20% acetic acid and extracted with peroxide-free ethyl ether. The ether solution was washed several times with water, then with 1% sodium carbonate, and finally with water until the washings were neutral. The yield of crude linolenaldehyde was 4.9 g. (86% based on the ester). This substance was found to be almost pure when examined by thin-layer chromatography. Small amounts of oxidized products were the only impurities.

The aldehyde was molecularly distilled at 150–160° C./2 mm. to yield 3.9 g. of a colorless liquid, which was chromatographically pure. The over-all yield with respect to the methyl linolenate was 68%. The 2,4-dinitrophenylhydrazone, crystallized from ethanol, had a melting point of 39.5–40.5°C. Reported: 40.0–40.5° C. (1)

Analyses: Calculated for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.35; H, 11.70.

Aldehydes from Menhaden Oil. When 5.0 g. (0.018 mole) of pure glycols from menhaden oil were cleaved with lead tetraacetate, 4.9 g. of aldehydes were obtained. This quantity represents an over-all yield of 87%, based on the starting methyl esters. These aldehydes, when examined by thin-layer chromatography, were found to be comparable in purity with the undistilled linolenaldehyde.

Spectral Analyses

The methyl linolenate contained 5–10% unsaturation in the *trans* form since it was prepared by the bromination-debromination technique. Methyl esters from menhaden oil contained only a trace amount of *trans* isomers, and infrared analyses of both aldehyde preparations indicated that there was essentially no increase during the synthesis. Only bands characteristic of C-H bonds, saturated and unsaturated carbon-to-carbon linkages, and aldehyde groups were found. No trimer was detected either by infrared analysis (9) or by thin-layer chromatography.

An ultraviolet analysis of the aldehydes indicated the presence of 5–6% conjugated diene and only a trace of higher conjugates in both products.

Discussion

It has been reported that such impurities as free fatty acids and hydroxyl compounds in the methyl esters lower the yield of acyloin (8). In the present work it was found that when 1% linolenic acid was added to methyl linolenate, the yield of acyloin was substantially reduced. Consequently the methyl esters must be entirely free of these impurities.

Small amounts of dione are formed in the condensation (1–3%). This compound may be seen at the solvent front of the chromatogram in Figure 1b, e. No attempt was made to remove this product since it is readily reduced to the glycol.

Owing to the instability of polyunsaturated aldehydes, any attempt to purify them by either column chromatography or fractional distillation is destructive and results in low yields. In order that aldehydes of high purity could be obtained, every effort was made to isolate the glycol in pure form. Therefore fatty acids not removed in the work-up of the crude acyloin may be removed on a silicic acid column prior to reduction with lithium aluminum hydride. If this is not done, separation of the resulting primary alcohols from the vicinal glycols is difficult. The chromatogram in Figure 2b shows that these compounds

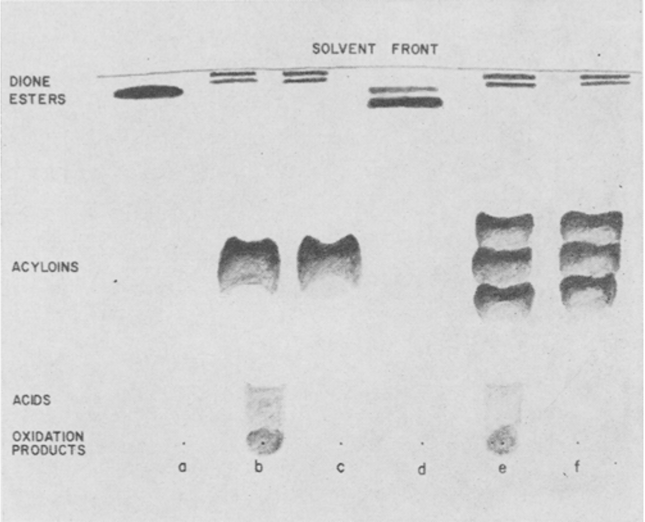

FIG. 1. Thin-layer silicic acid adsorption chromatogram of reactants and products in the acyloin condensation.

Solvent system: 90:10 petroleum ether (b.p. 30–60°C.) -ethyl ether

Development time: 30 min.

Indicator: Iodine vapors

a) Methyl linolenate, b) crude linolenoin containing fatty acids and dione, c) linolenoin with trace of dione, d) methyl esters from menhaden oil, e) crude acyloins from menhaden oil, showing fatty acids and a trace of dione, and f) acyloins from menhaden oil with trace of dione.

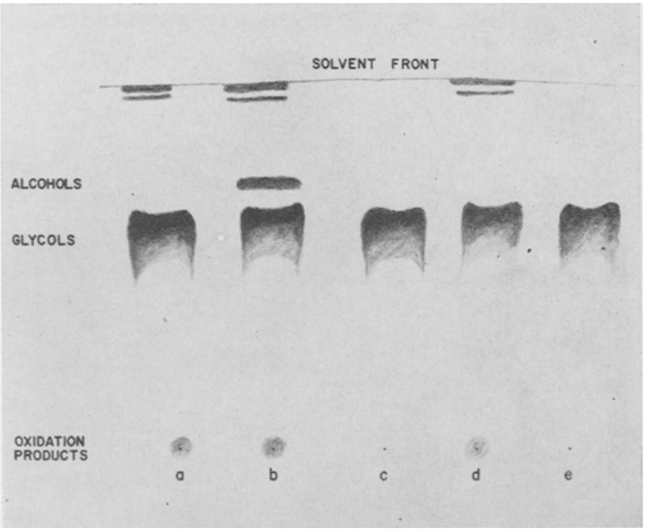

FIG. 2. Thin-layer silicic acid adsorption chromatogram of glycols.

Solvent system: 70:30:1 petroleum ether (b.p. 30–60°C.) -ethyl ether-acetic acid

Development time: 40 min.

Indicator: Iodine vapors

a) Crude hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol prepared from acid-free acyloins, b) crude hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol containing linolenyl alcohol and other impurities, c) pure hexatriconta-3,6,9,27,30,33-hexaene-18,19-diol, d) crude glycols from menhaden oil free of monoalcohols, and e) pure glycols from menhaden oil.

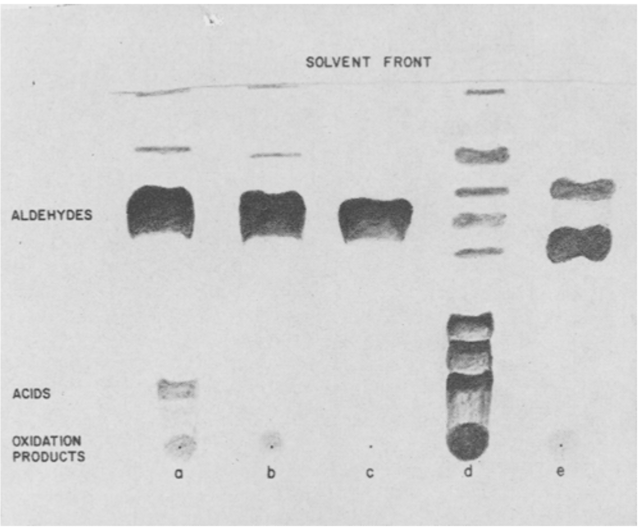

FIG. 3. Thin-layer silicic acid adsorption chromatogram of aldehydes.
Solvent system: 95:5 petroleum ether (b.p. 30–60°C.) -ethyl ether
Development time: 30 min.
Indicator: Iodine vapors
a) Crude linolenaldehyde containing fatty acids, b) undistilled linolenaldehyde, acid-free, c) distilled linolenaldehyde, d) pot residue from the distillation of linolenaldehyde showing products of thermal and oxidative decomposition, and e) undistilled aldehydes from menhaden oil, acid-free.

are only slightly segregated even by thin-layer chromatography, which gives more discrete separations than does column chromatography. Molecular distillation of crude linolenaldehyde improved the purity only slightly, as may be seen from the chromatogram shown in Figure 3b, c.

Methyl esters derived from menhaden oil exhibit subfractionation (Figure 1d) when chromatogrammed on thin layers of silicic acid (6). This phenomenon was observed in the present work with the acyloins and the aldehydes as well (Figures 1e, f; 3e).

Summary

The preparation of linolenaldehyde and of mixed aldehydes from highly unsaturated sources, such as menhaden oil *via* the acyloin condensation, is described. Reduction of the acyloins and subsequent cleavage of the glycols gave over-all yields of 85 to 90% free aldehydes.

The intermediates in the synthesis as well as the final products were analyzed in part by the novel method of thin-layer silicic acid chromatography.

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Sulfates of Ethoxylated Tridecyl Alcohol in Dishwashing Formulations[1]

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THE DEMAND for light-duty liquid detergents for household dishwashing has grown rapidly over the past few years. Present-day products are generally based on alkylaryl sulfonates, fortified with various auxiliary foam boosters. Sulfates of ethoxylated hydrophobes have found broad acceptance because of their ability to impart excellent foam stability to formulations, especially in the presence of greasy soil. In addition, they are relatively low in cost as compared with other competitive materials.

Earlier work in this field has been reported by Weil *et al.* (1), who investigated the performance of the sulfated ethoxylates of the tallow alcohols in the Ross-Miles foam test. These investigators also used a dishwashing test, based on the Terg-O-Tometer as developed by Leenerts (2), to measure the relative cleaning-power of a pure surfactant. They found that wetting time increased while foam height and the ability to clean dishes decreased with increasing ethylene oxide content.

Currently there are three important sources for sulfated ethoxylate derivatives. These are the alkylphenols, oxo-based tridecyl alcohol, and lauryl alcohol from fatty sources. The object of the work reported in this paper has been to compare the relative efficiencies of sulfated ethoxylates, in particular those based on tridecyl alcohol, as foam stabilizers in typical light-duty, liquid dishwashing formulations. The effect of both ethylene oxide to hydrophobe mole ratio and various sulfating agents has been established. Emphasis has been placed on a carefully controlled dishwashing procedure as the best available measure

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