Summary

1. Cinnamic aldehyde when heated with glycerol and a small amount of 40% sulfuric acid under reduced pressure readily condenses to give a pasty crystalline mixture of isomeric five- and six-membered cinnamylidene glycerols.

2. From the crude material a crystalline solid and an oil can be readily separated, the former of which is shown to be the six-membered acetal (1,1′-cinnamylidene glycerol) and the latter the five-membered derivative (1,2-cinnamylidene glycerol).

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OMEGA-HYDROXY ALIPHATIC ACIDS. SYNTHESIS OF SABINIC ACID

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In a previous research[2] it was shown that the ethyl esters of ω-aldehydo aliphatic acids could be prepared readily by the ozonization of various unsaturated esters. These substances are convenient intermediates for the preparation of the esters of ω-hydroxy aliphatic acids, since the aldehyde esters are quantitatively converted by means of hydrogen and platinum to the corresponding alcohols. By saponification the ω-hydroxy acids result. In this investigation the five compounds, 9-hydroxynonanoic, 10-hydroxydecanoic, 11-hydroxyundecanoic, 12-hydroxydodecanoic and 13-hydroxytridecanoic acids have been synthesized and studied.

$$\left.\begin{array}{l} CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \\ CH_2{=}CH(CH_2)_8CO_2CH_3 \\ CH_2{=}CH(CH_2)_9CO_2CH_3 \\ CH_2{=}CH(CH_2)_{10}CO_2CH_3 \\ CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2CH_3 \end{array}\right\} \begin{array}{l} \xrightarrow{O_3} CHO(CH_2)_xCO_2CH_3 \xrightarrow{2H} \\ CH_2OH(CH_2)_xCO_2CH_3 \longrightarrow CH_2OH(CH_2)_xCO_2H \end{array}$$

The ω-hydroxy acids are of interest from several standpoints: first, a number of them are naturally occurring compounds; second, they may be valuable intermediates for the synthesis of large-membered lactones and, third, they offer an opportunity to study the compounds formed by intermolecular esterification.

Among such acids isolated from natural sources which have been studied

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[1] This paper is an abstract of a thesis submitted by W. H. Lycan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Noller and Adams, This Journal, **48**, 1074 (1926); Tomecko and Adams, *ibid.*, **49**, 920 (1927); Davies and Adams, *ibid.*, **50**, 1749 (1928).

are sabinic and juniperic acids. These were extracted by Bougault[3] and the structures determined as 12-hydroxydodecanoic acid and 16-hydroxyhexadecanoic acid, respectively. The synthetic 12-hydroxydodecanoic acid, which melted at 83–84°, proved to be identical with the natural product, as determined by the melting point and mixed melting point with a sample of sabinic acid kindly furnished by Dr. Bougault. In a recent article by Bhattacharya, Saletore and Simonsen,[4] 12-hydroxydodecanoic acid was prepared as an intermediate in the course of another investigation. It was reported as melting at 78–79°. The method of synthesis might readily lead to the presence of impurities difficult to remove and the low melting point indicates this to be the case. During the preparation of this manuscript, a paper by Ruzicka and Stoll[5] has come to hand which describes ω-hydroxy acids containing 13 to 17 carbon atoms. The method of preparation used by them differed entirely from that used in this research and consisted in the saponification of the corresponding lactones produced in turn by the oxidation of the cyclic ketones. It was found that the 16-hydroxyhexadecanoic acid was identical with juniperic acid. Moreover, the melting point of the 13-hydroxytridecanoic acid proved to be identical with that obtained for the same acid in this investigation.

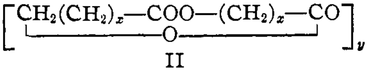
Large-membered lactone rings have been shown to occur naturally by Kerschbaum[6] who isolated the lactone of ambrettolic acid and of pentadecanolic acid from certain natural oils. Such ring compounds are also of considerable importance from a purely theoretical standpoint as they offer an opportunity to study quantitatively the relative stability of large rings. In the latest paper by Ruzicka,[5] our work along this line has been anticipated. He has prepared analogous large-membered lactones by oxidizing the corresponding cyclic ketones.

The study in this Laboratory is, therefore, being centered on the preparation of intermolecular esters from the hydroxy acids. These compounds, possible structures for which are represented by Formulas I and II, present an interesting field of polymeric-like substances which, on account of their properties, may readily be studied.

$$\mathrm{HO{-}[(CH_2)_x{-}COO{-}(CH_2)_x]_y{-}COOH}$$

I

or



$$\left[\mathrm{CH_2(CH_2)_x{-}COO{-}(CH_2)_x{-}CO}\right]_y$$

II

Bougault[3] believed that sabinic and juniperic acids probably existed in the plant in the form of such polymers which he designated as etholides.

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[3] Bougault and Bourdier, *Compt. rend.*, **147**, 1311 (1908); *J. pharm. chim.*, [6] **29**, 561 (1909); [6] **30**, 10 (1909); Bougault, *Compt. rend.*, **150**, 874 (1910); *J. pharm. chim.*, [7] **1**, 425 (1910); **3**, 101 (1911); Bougault and Cattelain, *Compt. rend.*, **186**, 1746 (1928).

[4] Bhattacharya, Saletore and Simonsen, *J. Chem. Soc.*, 2678 (1928).

[5] Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

[6] Kerschbaum, *Ber.*, **60**, 902 (1927); German Patent application 105,677.

Ruzicka[5] noticed by-products in the oxidation of the cyclic ketones which he assumed to be etholides. One of these he purified and by analysis showed it to be a dimolecular compound. In this investigation the 9-hydroxynonanoic acid was heated and converted into a well-crystallized polymer melting at 64–66°, which analyzed also for a dimolecular compound. It has not yet been determined whether the molecule consists of a simple dimolecular lactone, a polymer of such a lactone or a very long, open-chain compound in which the free hydroxyl and carboxyl groups have practically no effect on the analysis. It is readily saponified by aqueous potassium hydroxide to the simple hydroxy acid. A more quantitative study of these substances and their derivatives will be reported in a subsequent paper.

Experimental Part

Methyl Esters of ω-Aldehydo Aliphatic Acids.—The method of preparation of the methyl esters of the ω-aldehydo acids and the unsaturated esters from which they are made has been described in previous papers.[2] The ozonizations of the methyl esters of 11,12-dodecenoic acid and 12,13-tridecenoic acid have not been as fully described as those of the other unsaturated acids used in these syntheses. In this communication are described the by-products obtained in the two ozonizations mentioned, the monomethyl esters of nonane-1,9-dicarboxylic acid and decane-1,10-dicarboxylic acid, respectively, isolated from the residues remaining after the distillation of the corresponding aldehyde esters.

Monomethyl Ester of Decane-1,10-dicarboxylic Acid.—The residue from the distillation of ω-aldehydo-undecanoate was recrystallized six times from petroleum ether (b. p. 50–60°) and melted at 51.5–52°.

Anal. Subs., 0.1784: CO_2, 0.4692; H_2O, 0.1953. Calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.91. Found: C, 63.73; H, 9.94.

Nonane-1,9-dicarboxylic acid, m. p. 109–110°, and decane-1,10-dicarboxylic acid, m. p. 126.5–127°, were obtained by the hydrolysis of the monomethyl esters with 10% aqueous sodium hydroxide solution and subsequent acidification.

Semicarbazone of Methyl 11-Aldehydo-undecanoate.—The semicarbazone was prepared by shaking equal weights of the aldehyde ester and semicarbazide sulfate with twice the weight of sodium acetate in dilute alcohol solution. The semicarbazone was recrystallized several times from ethyl acetate; m. p. 90–92°.

Anal. Subs., 0.1659: CO_2, 0.4179; H_2O, 0.1953. Calcd. for $C_{14}H_{28}O_3N_3$: C, 58.70; H, 9.84. Found: C, 58.36; H, 9.50.

Methyl Esters of the ω-Hydroxy Aliphatic Acids.—The methyl esters of the ω-aldehydo acids were reduced to the corresponding methyl esters of the ω-hydroxy acids according to the method of Carothers and Adams[7] for the reduction of aldehydes to primary alcohols. A solution of 0.2 mole of the aldehyde ester in 100 cc. of 95% ethyl alcohol, to which had been added 0.2 g. of platinum oxide catalyst and 2 cc. of freshly prepared 0.1 *M* ferrous sulfate solution, was shaken with hydrogen under about 2.5–3 atm. pressure. Usually about two hours were required for the absorption of the theoretical quantity of hydrogen. The solution was then filtered to remove the platinum black and the alcohol was removed on a steam-bath. The hydroxy ester was dissolved in 350 cc. of ether and the ether solution was washed, first with 150 cc. of 20% sodium

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[7] Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923).

bisulfite solution, then with 150 cc. of 10% sodium carbonate solution and finally with 500 cc. of water. The ether solution was then dried with anhydrous magnesium sulfate. The alcohol esters were finally distilled under diminished pressure. The yields were from 80–90% of the theoretical.

TABLE I

METHYL ESTERS OF ω-HYDROXY ACIDS

	Unsaturated ester	ω-Hydroxy ester	B. p., °C. (3 mm.)	M. p., °C.	n_D	d^{20}
1	Methyl oleate	$CH_2OH(CH_2)_7CO_2CH_3$	137–139	.....	1.4438	0.9588
2	Methyl undecenoate	$CH_2OH(CH_2)_8CO_2CH_3$	145–147	.....	1.4471	.9618
3	Methyl dodecenoate	$CH_2OH(CH_2)_9CO_2CH_3$	156–159	.....	1.4493	.9542
4	Methyl tridecenoate	$CH_2OH(CH_2)_{10}CO_2CH_3$	164–166	34–35	....	....
5	Methyl erucate	$CH_2OH(CH_2)_{11}CO_2CH_3$	170–173	40.5–41.5	....	....

ANALYSES

	Subs., g.	CO_2, g.	H_2O, g.	Calcd., %		Found, %	
				C	H	C	H
1	0.2270	0.5337	0.2204	63.80	10.71	64.20	10.86
2	.1792	.4255	.1746	65.28	10.96	64.76	10.89
3	.1969	.4788	.1934	66.60	11.19	66.32	10.97
4	.1825	.4517	.1875	67.76	11.38	67.50	11.44
5	.2000	.4796	.1908	68.85	11.56	68.55	11.67

Phenyl Urethans of the Methyl Esters of the ω-Hydroxy Acids.—The phenyl urethans of the methyl esters of the ω-hydroxy acids were prepared by mixing the ester with one-third its weight of phenyl isocyanate. The reaction was ordinarily spontaneous and was hastened by gentle warming on a hot-plate. The mixture was allowed to stand for one hour, after which the product was purified by repeated crystallizations from petroleum ether or mixtures of benzene and petroleum ether (b. p. 50–60°).

TABLE II

PHENYL URETHANS OF THE METHYL ESTERS OF ω-HYDROXY ACIDS

	Formula	M. p., °C. (corr.)	Analyses Calcd., %		Found, %	
			C	H	C	H
1	$C_6H_5NHCO_2(CH_2)_8CO_2CH_3$	53–54	66.40	8.20	66.15	8.42
2	$C_6H_5NHCO_2(CH_2)_9CO_2CH_3$	54–55	67.24	8.47	67.08	8.50
3	$C_6H_5NHCO_2(CH_2)_{10}CO_2CH_3$	64.5–65.5	68.01	8.72	68.14	8.81
4	$C_6H_5NHCO_2(CH_2)_{11}CO_2CH_3$	64–65	68.76	8.95	68.54	8.79
5	$C_6H_5NHCO_2(CH_2)_{12}CO_2CH_3$	73.5–74	69.45	9.16	69.34	9.24

ω-Hydroxy Aliphatic Acids.—The methyl esters of the ω-hydroxy acids were hydrolyzed with a 10% excess of 10% aqueous potassium hydroxide solution. The hydrolysis of 0.1 mole of the ester required about two and one-half hours. When solution was complete the water was removed by evaporation on the steam-bath and the potassium salts thus obtained were crystallized three times from absolute ethyl alcohol. The potassium salts crystallized as fluffy white crystals which analyzed for the theoretical percentage of potassium. The pure salt was dissolved in a small amount of water and evaporated on a steam-bath to remove traces of alcohol. It was again dissolved in water and the acid was freed by titration to Congo Red paper with 1 *N* hydrogen chloride solution. The acid which separated as a gelatinous precipitate was extracted with ether, the ether solution washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under diminished pressure at ordinary temperatures and the resulting acids were purified by careful crystallization.

The compounds were dissolved in hot ethyl acetate and immediately cooled in an ice- and salt-bath. Crystallization in the usual way resulted in the formation of a small amount of insoluble polymeric material.

TABLE III

ω-HYDROXY ACIDS

	Formula	M. p., °C. (corr.)	Analyses Calcd., % C	H	Found, % C	H
1	$CH_2OH(CH_2)_7CO_2H$	53–54	62.07	10.43	62.30	10.67
2	$CH_2OH(CH_2)_8CO_2H$	75–76	63.77	10.72	63.56	10.75
3	$CH_2OH(CH_2)_9CO_2H$	65.5–66	65.29	10.96	65.36	10.83
4	$CH_2OH(CH_2)_{10}CO_2H$	83–84	66.59	11.20	65.50	11.20
5	$CH_2OH(CH_2)_{11}CO_2H$	77–78	67.82	11.39	67.88	11.39

Polymer of 9-Hydroxynonanoic Acid.—When 9-hydroxynonanoic acid was heated at a pressure of 3 mm. for half an hour at 220–230°, water was eliminated and a polymer-like product was obtained. This substance was crystallized from a mixture of benzene and petroleum ether (b. p. 50–60°) and was obtained as a fluffy, white, finely-divided powder; m. p. 64–66°.

Anal. Subs., 0.1921, 0.1898; CO_2, 0.4852, 0.4793; H_2O, 0.1774, 0.1765. Calcd. for $(C_9H_{16}O_2)_x$: C, 69.18; H, 10.33. Found: C, 68.88, 68.86; H, 10.33, 10.40.

This compound was insoluble in the cold in ethyl alcohol, petroleum ether, acetone and ethyl acetate, but was soluble in the hot. It was insoluble in cold aqueous potassium hydroxide solution. Upon warming with 10% aqueous potassium hydroxide solution on a steam-bath for one hour hydrolysis was complete. The potassium salt was crystallized from absolute alcohol and the acid freed as before was identical with the 9-hydroxynonanoic acid.

Molecular weight determinations in benzene both by boiling-point and freezing-point methods gave such variable results that more reliable data are needed before publication.

Summary

1. A general method is given for the preparation of ω-hydroxy esters and ω-hydroxy acids by reduction of the aldehydo esters obtained upon ozonization of the methyl esters of unsaturated acids.

2. A polymer of one of these ω-hydroxy acids is described.

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