[Communication from the Department of Industrial and Cellulose Chemistry, McGill University]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXII. THE ISOMERIC CINNAMYLIDENE GLYCEROLS

By Harold Hibbert and Myron S. Whelen[1]

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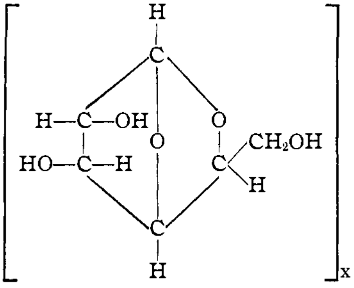
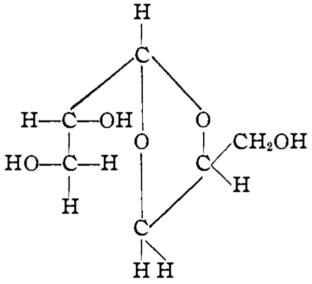
The properties of cyclic acetals and the nature of cyclic acetal formation in relation to carbohydrates and polysaccharides have been repeatedly emphasized in the course of this series of communications. Of added interest is the close connection for example, between cellulose, considered as an anhydro glucose (I) (a suggestion first put forward by one of us)[2] and 1,2-dihydroxypropylidene glycerol (II).[3]



I



II

For this reason it becomes highly desirable to synthesize such derivatives as 1,2-dihydroxypropylidene glycerol (II) and glycol, in order to

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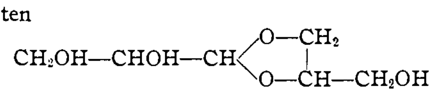
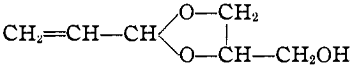
[2] Hibbert, *Chem. Met. Eng.*, **22**, 838 (1920). The constitution of cellulose was discussed at length in a later communication [Hibbert, *Ind. Eng. Chem.*, **13**, 256, 334 (1921)] in which the view was taken that no decision could be reached as to whether this substance was to be regarded as a polymerized (or associated) anhydroglucose or as a very large ring compound. The question still remains an open one, as is evident from the recent discussions on this subject [Bergmann, Herzog and Jancke, *Naturwissenschaft.*, **16**, 464 (1928); Kurt Hess and Carl Trogus, *Ber.*, **61**, 1982 (1928); Meyer and Mark, *Ber.*, **61**, 593 (1928)]; Kurt Meyer, *Z. ang. Chem.*, **41**, 935 (1928); Sponsler and Dore, "Colloid Symposium Monograph," **4**, 174 (1926); This Journal, **50**, 1940 (1928); Katz, "*Ergebn. exakt. Naturwiss.*" **3**, 363, J. Springer, Berlin, (1924); **4**, 185 (1928); Haworth, *Helv. Chim. Acta*, **11**, 534 (1928). The extensive chemical investigations carried out by Kurt Hess in this field—an excellent summary of which is to be found in his recent valuable textbook on "Cellulose Chemistry"—provide, in the writers' opinion, considerable support for the theory that cellulose may be an associated form of an anhydro-dextrose building unit.

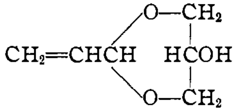
[3] The formula is more customarily written



$$CH_2OH{-}CHOH{-}CH\begin{matrix}\diagup O{-}CH_2\\ \quad\;\; |\\ \diagdown O{-}CH{-}CH_2OH\end{matrix}$$

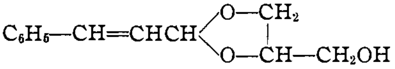
ascertain how far such structures exhibit a tendency toward polymerization or association.[4] The simplest mode of synthesis of these products appeared to lie in the primary preparation of cyclic acetals from unsaturated aldehydes (acrolein, crotonaldehyde, cinnamic aldehyde) and glycerol. Isolation of the two structurally isomeric acetals, for example (III) and (IV)

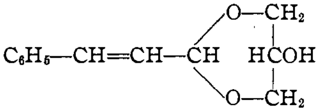

III


IV

could then be followed by conversion of (III) into the corresponding dihydroxy compound, *viz.*, dihydroxypropylidene glycerol (II).

Both acrolein and cinnamic aldehyde condense readily with glycerol, the former without the use of a catalyst. The present paper deals with the isolation, identification and properties of the two structurally isomeric cinnamylidene glycerols (V) and (VI).


V


VI

The only literature reference to cinnamylidene glycerol is a short communication by Peacock[5] in which he states this product may be "readily obtained as a viscous oil, which slowly solidifies to a mass of crystals, m. p. 110–112°," but gives no directions as to its preparation. He pointed out that the cinnamylidene group and the carbinol group may exhibit *cis-trans* isomerism with respect to the heterocyclic rings and that in addition to this possibility of isomerism there is also that due to the double linking in the cinnamylidene group, which may again cause the formation of *cis* and *trans* isomerides. The number of possible isomerides for each formula is therefore four, neglecting optically active members. Peacock only isolated a single isomer, the structure of which was left unsolved, and gave no indication of a belief in the possibility of *simultaneous* formation of *both* ring structures such as is demanded by the Michael partition principle.

Previous work carried out in this field[6] shows that in the condensation of a saturated aldehyde with glycerol, a partition between the 1,1′- and 1,2-hydroxyl groups always occurs, resulting in the formation of two structural ring isomers, *viz.*, a five- and a six-membered cyclic acetal, respectively. Peacock in his work apparently only expected to find a one-ring system. The simultaneous formation of both types is now shown to

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[4] The synthesis of dihydroxypropylidene glycol has now been accomplished and that of dihydroxypropylidene glycerol is in progress.

[5] Peacock, *J. Chem. Soc.*, **107**, 816 (1915).

[6] Hibbert and co-workers, THIS JOURNAL, **50**, 2235, 2242 (1928).

be true in the cases of cinnamic aldehyde and the isolation and properties of two structural isomeric ethers (five- and six-membered ring isomers) of cinnamylidene glycerol are described in the experimental part. The process outlined serves as a convenient method for the synthesis of these somewhat inaccessible products.

In the condensation of cinnamic aldehyde and glycerol the crude cinnamylidene glycerol is left as a viscous oil which slowly solidifies in about twenty-four hours to a thick pasty mass of crystals, readily separable from the accompanying oil. Purification of the crystals, followed by methylation and hydrolysis, yields glycerol β-methyl ether, thus identifying the ring structure as the six-membered acetal (VI). The oil[7] remaining after the removal of the crystalline isomer and the unchanged cinnamic aldehyde, on similar treatment, yields glycerol α-methyl ether, thus serving to identify it as the five-membered acetal (V). It is of interest that the methyl ethers of both the 1,2- and 1,1′-cinnamylidene glycerols are very sensitive to hydrolysis (involving ring scission), much more so in fact than the free acetals. This is in agreement with observations made by Irvine, Macdonald and Soutar[8] on *iso*propylidene glycerol.

Only one of the numerous possible isomers of each of the structural five- and six-membered cinnamylidene glycerols was isolated, due possibly to the labile character of the other forms, although no special effort was made to investigate this phase of the problem, the direct object being to prove the simultaneous formation of both types of structural ring isomerism.

Investigations dealing with the action of benzoyl hydroperoxide on the cinnamylidene glycerols and the synthesis of phenyl 1,2-dihydroxypropylidene glycerol are in progress.

Experimental

Preparation and Isolation of the Isomeric Cinnamylidene Glycerols.—One hundred and thirty-two g. (1 mole) of pure cinnamic aldehyde, 92 g. of glycerol and five drops of 40% sulfuric acid were heated together with constant shaking by hand in a round-bottomed pyrex flask under a pressure of 20 mm. At approximately 50° water began to distil over. At the same low pressure the temperature was gradually raised during the course of approximately twenty-five minutes to 100°, at which it was maintained for thirty minutes, or until there was complete miscibility and water ceased to be given off. The reaction product was a viscous oil which slowly solidified after about twenty-four hours to a thick, pasty mass of crystals, the pasty mass containing a considerable quantity of an adhering oil. This product was disintegrated and thoroughly washed with water at 30° to remove unchanged glycerol and sulfuric acid, then filtered and pressed as dry as possible on a suction filter, the solid remaining as a thick, pasty mass. This was dissolved in warm benzene, separated from water in a separatory funnel and the warm benzene solution dried by shaking with anhydrous sodium sulfate. On filtering the hot solution and cooling, yellowish-white crystals separated out which

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[7] It was not found possible to isolate this product in a sufficiently pure state for analysis.

[8] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

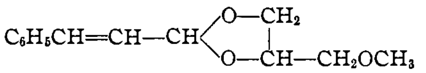
on recrystallization from benzene yielded 38 g. of long, asbestos-like needles, m. p. 121°.

Anal. Subs., 0.1557: CO_2, 0.4004; H_2O, 0.090. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.79. Found: C, 70.08; H, 6.54. Molecular weight determinations carried out in ethylene bromide gave values ranging from 238–260; theoretical, 206.

Attempts to crystallize the unpurified oil obtained after the removal of the above solid were futile. Distillation under reduced pressure was unsatisfactory, yielding only a portion of unchanged cinnamic aldehyde and a small amount of oil, b. p. 200–225° (6 mm.), which solidified on cooling. This solid was identified as 1,1′-cinnamylidene glycerol which had not been removed by crystallization. The bulk of the mother liquor remained as a gummy product and, as shown later, consisted of the 1,2-cinnamylidene glycerol.[7]

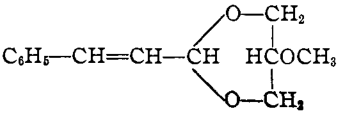
During the course of this investigation the very labile character of these carbon–oxygen cyclic structures was observed, in that samples of the solid 1,1′-cinnamylidene glycerol, m. p. 121°, slowly changed on standing into an oily liquid. From analogy with the corresponding benzylidene glycerols[9] this was presumably due to an interconversion of one isomeric form into the other, but the product was not investigated.

Determination of Structure.—The methylation hydrolysis method of Irvine and co-workers was followed in order to determine the identification of the isomeric cinnamylidene glycerols. Methylation with silver oxide and methyl iodide gave the corresponding cinnamylidene glycerol methyl ethers (VII) and (VIII)



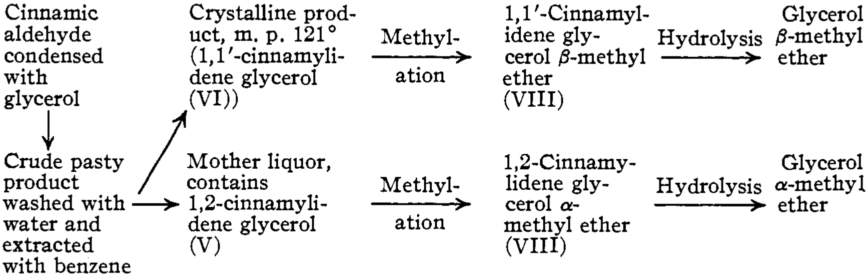
$$C_6H_5CH{=}CH{-}CH\begin{matrix}\diagup O{-}CH_2\\ \phantom{\diagup O{-}}|\\ \diagdown O{-}CH{-}CH_2OCH_3\end{matrix}$$

VII



VIII

the crystalline 1,1′-cinnamylidene glycerol (VI) (m. p. 121°) giving exclusively the crystalline 1,1′-cinnamylidene glycerol β-methyl ether (VIII), and the mother liquor from the original condensation reaction, after removal of the acetal (VI) yielding the liquid 1,2-cinnamylidene glycerol α-methyl ether (VII). Hydrolysis of the latter product gave glycerol α-methyl ether, while hydrolysis of the former yielded glycerol β-methyl ether as indicated in the following scheme



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[9] Hill, Whelen and Hibbert, THIS JOURNAL, 50, 2235 (1928).

No trace of the crystalline β-methyl ether (VIII) was found in the methylation product obtained from the liquid acetal (V) although it is admittedly impossible to remove all of the solid acetal (VI) from the liquid acetal (V) by crystallization.

Synthesis of 1,1'-Cinnamylidene Glycerol β-Methyl Ether (VIII).—Thirty-three grams of crystalline 1,1'-cinnamylidene glycerol (VI) was methylated in the usual manner, using 60 g. of silver oxide and 115 g. of methyl iodide. The reaction mixture was thoroughly extracted with warm benzene from which, on partial evaporation and cooling, 1,1'-cinnamylidene glycerol β-methyl ether (VIII) separated, mixed with a small amount of unchanged 1,1'-cinnamylidene glycerol. Fractional recrystallization from benzene, with final recrystallization from ligroin (b. p. 80–90°), yielded 13 g. of white, pearly leaflets, m. p. 79–80°. The only other substance isolated was 4.8 g. of white needles, m. p. 115–118°. A mixed melting point determination with approximately equal quantities of this substance and 1,1'-cinnamylidene glycerol (m. p. 121°) gave a m. p. of 119°, showing these substances to be identical.

Anal. (1,1'-Cinnamylidene Glycerol β-Methyl Ether.) Subs., 0.1596: CO_2, 0.4180; H_2O, 0.970. Calcd. for $C_{13}H_{16}O_3$: C, 70.86; H, 7.33. Found: C, 71.43; H, 6.80.

Hydrolysis of 1,1'-Cinnamylidene Glycerol β-Methyl Ether (VIII).—Sixteen g. of crystalline cinnamylidene glycerol β-methyl ether was hydrolyzed by boiling under a reflux condenser for seventy minutes with 150 cc. of 75% aqueous ethyl alcohol containing 0.5% of hydrochloric acid. Fifty cc. of water was then added and the alcohol removed under reduced pressure.

The considerable quantity of cinnamic aldehyde present was separated in a separatory funnel from the hydrolysis product and the latter extracted with ether. The aqueous solution was then neutralized with lead carbonate, filtered and concentrated under reduced pressure. The residual oil on distillation yielded 3.8 g. of glycerol β-methyl ether, b. p. 123° (13 mm.); $n_D^{17°}$, 1.4497.[8]

Anal. Subs., 0.1345: CO_2, 0.2208; H_2O, 0.1119. Calcd. for $C_4H_{10}O_3$: C, 45.28; H, 9.45. Found: C, 44.78; H, 9.26.

Methylation of 1,2-Cinnamylidene Glycerol.—The benzene solution obtained after removal of the crystalline 1,1'-cinnamylidene glycerol (p. 623) was concentrated in order to remove the solvent and thirty grams of the residual mother liquor containing the 1,2-cinnamylidene glycerol was then methylated in the usual manner with 60 g. of silver oxide and 115 g. of methyl iodide. The reaction mixture was extracted with benzene, the solvent evaporated and the residual oil fractionated. It yielded 9.4 g. of cinnamic aldehyde and 13.2 g. of 1,2-cinnamylidene glycerol α-methyl ether, b. p. 164–166° (6 mm.); $n_D^{20°}$, 1.5455.

Attempts to obtain a satisfactory analysis were unsuccessful due to the ease of hydrolysis and difficulties in combustion of the material. As indicated below, however, its identity was definitely established by its hydrolysis into glycerol α-methyl ether.

Hydrolysis of Cinnamylidene Glycerol α-Methyl Ether.—Twelve g. of cinnamylidene glycerol methyl ether, on hydrolysis by the same method as used for the β-derivative, yielded 3.6 g. of glycerol α-methyl ether, b. p., 110° (13 mm.); $n_D^{17°}$, 1.4435.

Anal. Subs., 0.1588: CO_2, 0.2609; H_2O, 0.1291. Calcd. for $C_4H_{10}O_3$: C, 45.23; H, 9.45. Found: C, 44.80; H, 9.09.

Ease of Hydrolysis of the Cinnamylidene Glycerols and Ethers.—When compared with the methylidene and benzylidene glycerols and their corresponding ethers, the cinnamylidene glycerol derivatives exhibit a very much more pronounced tendency toward hydrolysis.

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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[Contribution from the Chemical Laboratory of the University of Illinois]

OMEGA-HYDROXY ALIPHATIC ACIDS. SYNTHESIS OF SABINIC ACID

By W. H. Lycan[1] and Roger Adams

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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.

$$\left.\begin{array}{l} \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3} \\ \mathrm{CH_2{=}CH(CH_2)_8CO_2CH_3} \\ \mathrm{CH_2{=}CH(CH_2)_9CO_2CH_3} \\ \mathrm{CH_2{=}CH(CH_2)_{10}CO_2CH_3} \\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2CH_3} \end{array}\right\} \xrightarrow{\mathrm{O_3}} \mathrm{CHO(CH_2)_{\mathit{x}}CO_2CH_3} \xrightarrow{\mathrm{2H}} \mathrm{CH_2OH(CH_2)_{\mathit{x}}CO_2CH_3} \longrightarrow \mathrm{CH_2OH(CH_2)_{\mathit{x}}CO_2H}$$

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).