

solution was cooled. The crystals were separated and recrystallized from hot water.

The purified product melted with decomposition at 246°. It was only slightly soluble in cold water and in alcohol, but soluble in both of these solvents at higher temperatures. It was insoluble in diethyl ether and ethyl acetate. Analysis showed it to have the expected composition.

*Anal.* Calcd. for  $C_{16}H_{24}O_4N_4$ : C, 55.52; H, 7.46; N, 17.28. Found: C, 55.36, 55.69; H, 7.38, 7.51, N (Jamieson), 17.28, 17.27.

**Acknowledgment.**—The authors wish to express their appreciation at this time to R. E. Kirk for the interest he has shown in this investigation and for the many helpful suggestions he has made.

### Summary

1. A method has been developed for isolating shellolic acid from various lacs. This method was based upon a modification of the procedure used

by Weinberger and Gardner for "laccollic lactone."

2. The various preparations of dimethyl shellolate obtained by this method were identical in properties with those described by Harries and Nagel.

3. It was shown that the total amount of shellolic acid in lac probably does not exceed 3.5 to 4%. This was about half of the fraction of acids whose lead salts are insoluble in alcohol.

4. "Laccollic lactone" was shown to be a mixture of dibasic acids. The resin fractions from which this product was obtained contained less shellolic acid than lac resin as a whole. This was interpreted as a further indication that other dibasic acids are also present as constituents of the interesters of lac resin.

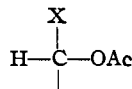
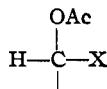
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## Derivatives of the Aldehydol Form of Sugars. IV<sup>1</sup>

BY M. L. WOLFROM AND ROBERT L. BROWN

In previous communications from this Laboratory<sup>1</sup> there have been reported a number of acyl halide carbonyl addition compounds of *aldehydo*-sugar acetates. In no instance, however, were these substances isolated in the two forms predictable on stereochemical grounds.



Such a pair of isomers has now been obtained in the *d*-galactose structure. Their specific rotations in chloroform solution are +62° and -44° and an appreciable rotation difference is thus exhibited. This rotation difference is in contrast with the very small ones noted<sup>1c</sup> in other pairs of acyclic isomers likewise differing only in the configuration of carbon one. The substances will be designated<sup>1c</sup>  $\alpha$ -1-chloro-*aldehydo-d*-galactose hexaacetate (+62°) and  $\beta$ -1-chloro-*aldehydo-d*-galactose hexaacetate (-44°).

This pair of acyclic  $\alpha, \beta$ -isomers was obtained by application to the previously reported  $\beta$ -isomer<sup>1a</sup> of the zinc chloride interconversion pro-

cedure of Hudson and co-workers.<sup>2</sup> Both isomers exhibited a stable rotation in acetyl chloride solution but on the addition of a small amount of zinc chloride they underwent an interconversion at room temperature to an equilibrium mixture containing approximately 76.5% of the alpha isomer and 23.5% of the beta isomer. This composition is calculated upon the reasonable assumption that only these two substances are present in the equilibrium mixture. It was noted that a four-fold increase in the concentration of zinc chloride used caused no significant shift of the equilibrium point. The same equilibrium was attained when *aldehydo-d*-galactose pentaacetate was treated under the same conditions. In acetyl chloride alone, *aldehydo-d*-galactose pentaacetate underwent a slow rotation change in the opposite direction. These rotation characteristics are diagrammed in Fig. 1.

The above interconversion conditions were likewise applied to the one known form of 1-chloro-*aldehydo-d*-glucose hexaacetate<sup>1b</sup> and to *aldehydo-d*-glucose pentaacetate and similar optical characteristics were observed (Fig. 2). Unfortunately, the  $\alpha$ -isomer in the *d*-glucose struc-

(1) Previous publications in this series: (a) M. L. Wolfrom, *THIS JOURNAL*, **57**, 2498 (1935); (b) M. L. Wolfrom and M. Konigsberg, *ibid.*, **60**, 288 (1938); (c) M. L. Wolfrom, M. Konigsberg and F. B. Moody, *ibid.*, **62**, 2343 (1940).

(2) Edna M. Montgomery, R. M. Hann and C. S. Hudson, *ibid.*, **59**, 1124 (1937).

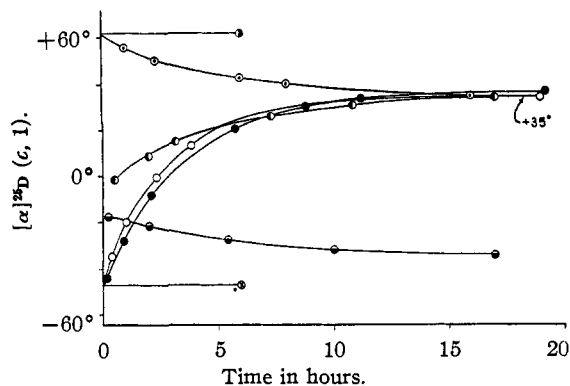


Fig. 1.—Mutarotation characteristics of  $\alpha$ - (I) and  $\beta$ -1-chloro-*aldehyde-d-galactose* hexaacetate (II) in acetyl chloride solution.  $\bullet$ , I in AcCl;  $\otimes$ , II in AcCl;  $\circ$ , I in AcCl containing 0.065% ZnCl<sub>2</sub>;  $\circ$ , II in AcCl containing 0.065% ZnCl<sub>2</sub>;  $\bullet$ , II in AcCl containing 0.26% ZnCl<sub>2</sub>;  $\ominus$ , *aldehyde-d-galactose* pentaacetate (III); in AcCl (*c* calcd. on basis I equivalent);  $\ominus$ , III (*c* calcd. on basis I equivalent) in AcCl containing 0.065% ZnCl<sub>2</sub>.

ture was not amenable to crystallization. The upward mutarotation in the acetyl chloride-zinc chloride mixture exhibited by the previously reported crystalline isomer, definitely characterizes it as the  $\beta$ -form.

### Experimental

**$\alpha$ -1-Chloro-*aldehyde-d-galactose* Hexaacetate.**—To a solution of 10 g. of *aldehyde-d-galactose* pentaacetate<sup>3</sup> in 150 cc. of acetyl chloride was added 4 cc. of a 10% solution of freshly fused zinc chloride in glacial acetic acid (containing a few drops of acetic anhydride). After standing for fifteen hours at room temperature (20–25°) the solution was poured with stirring into 3 liters of ice and water. The crude product was removed by filtration and washed with water; yield 10 g., m. p. 140–145°. This material was dissolved in hot acetone (decolorizing charcoal) and crystallized by the addition of water; yield 8.9 g., m. p. 145–150°. Fractional crystallization from absolute ethanol yielded a small amount of the less soluble and previously reported  $\beta$ -isomer<sup>1a</sup> and 2.3 g. (m. p. 152–153°) of the new isomer. Pure material was obtained on further crystallization from relatively large amounts of absolute ethanol; m. p. 153–154°, spec. rot. +62° (22°, *c* 2.5, abs. CHCl<sub>3</sub>, D-line), spec. rot. +60° (23°, *c* 1, CH<sub>3</sub>COCl, D-line). The recorded<sup>1a</sup> constants for the  $\beta$ -isomer are: m. p. 174–175°, spec. rot. –44° (CHCl<sub>3</sub>). The specific rotation of the  $\beta$ -isomer in acetyl chloride was found to be –47° (22°, *c* 1, D-line). Neither isomer exhibited any mutarotation in these solvents. The mutarotation characteristics in acetyl chloride solution (with and without zinc chloride) of both isomers and of *aldehyde-galactose* pentaacetate are diagrammed in Fig. 1.

The  $\alpha$ -isomer crystallized in colorless, elongated prisms that were soluble in chloroform, acetone and benzene; moderately so in acetyl chloride, ethanol and ether; and

(3) M. L. Wolfrom, *This Journal*, **52**, 2464 (1930); M. L. Wolfrom and M. Konigsberg, *ibid.*, **61**, 574 (1939).

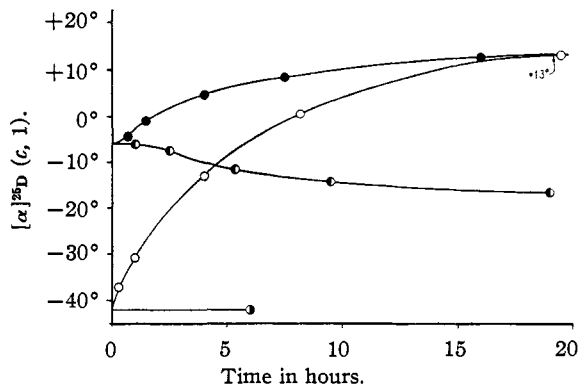


Fig. 2.—Mutarotation characteristics of  $\beta$ -1-chloro-*aldehyde-d-glucose* hexaacetate (I) in acetyl chloride solution.  $\bullet$ , I in acetyl chloride;  $\ominus$ , *aldehyde-d-glucose* pentaacetate (II) in acetyl chloride (*c* calcd. on basis I equivalent);  $\circ$ , I in acetyl chloride containing 0.065% ZnCl<sub>2</sub>;  $\bullet$ , II (*c* calcd. on basis I equivalent) in acetyl chloride containing 0.065% ZnCl<sub>2</sub>.

practically insoluble in water and petroleum ether. It was in general more soluble than the  $\beta$ -isomer.

*Anal.* Calcd. for C<sub>6</sub>H<sub>7</sub>O<sub>6</sub>(CH<sub>3</sub>CO)<sub>6</sub>Cl: Cl, 7.56; saponification value (seven equivalents), 14.9 cc. 0.1 N NaOH per 100 mg. Found: Cl, 7.54; saponification value, 15.0 cc.

The  $\alpha$ -isomer (1.2 g. of m. p. 151–152°) was obtained in a similar manner from an equilibrated mixture obtained from the  $\beta$ -isomer (2.5 g.), acetyl chloride (150 cc.) and 1.5 cc. of a 10% solution of freshly fused zinc chloride in glacial acetic acid (containing a few drops of acetic anhydride).

The halogen in both of these isomers exhibits a surprising stability and they were recovered unchanged on refluxing for several hours with absolute ethanol or benzene in the presence of an excess of silver carbonate.

**Action of Zinc Chloride-Acetyl Chloride on  $\beta$ -1-Chloro-*aldehyde-d-glucose* Hexaacetate.**—The mutarotation characteristics in acetyl chloride solution (with and without zinc chloride) of the one known isomer of 1-chloro-*aldehyde-d-glucose* hexaacetate<sup>1b</sup> are diagrammed in Fig. 2. Attempts to isolate the  $\alpha$ -isomer in crystalline condition were unsuccessful although dextrorotatory sirups were obtained. The  $\beta$ -isomer was isolated from the equilibrium mixture. The specific rotation of the  $\beta$ -isomer in acetyl chloride solution was found to be –42° (24°, *c* 1, D-line).

### Summary

1.  $\beta$ -1-Chloro-*aldehyde-d-galactose* hexaacetate has been converted into the  $\alpha$ -isomer by a solution of zinc chloride in acetyl chloride and the course of this interconversion has been followed polarimetrically.

2. The mutarotation characteristics of 1-chloro-*aldehyde-d-glucose* hexaacetate in a solution of acetyl chloride containing zinc chloride have been determined and characterize this substance as a  $\beta$ -form.