determined empirically to be the best for a speedy reaction and a pure product.

Proof of Structure of V.—When V was desulfamidated by 75% sulfuric acid in the manner described for the analogous dibromo compound,[7] a 51% yield of 2,6-dichloroaniline, m. p. 38–39° (recorded 39°), could be steam distilled from the reaction mixture. This was acetylated with acetic acid and acetyl chloride,[8] m. p. 178.5–179°, recorded 175°, after recrystallization from 25% acetic acid.

Summary

1. On oxidation sulfanilamide yields the corresponding azo- and azoxy-benzenes which may be reduced to the hydrazo compound.

2. It can be chlorinated readily by a mixture of hydrogen peroxide and hydrochloric acid.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 13, 1940

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[7] Fuchs, *Monatsh.*, **36**, 125 (1915).

[8] Beilstein and Kurbatow, *Ann.*, **196**, 215, 219–220 (1879).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF WISCONSIN]

The Mutarotation and Rotatory Dispersion of Derivatives of Aldehydo-*d*-galacturonic Acid[1]

BY ROBERT J. DIMLER AND KARL PAUL LINK

Aldehydo tetraacetyl methyl-*d*-galacturonate and one of its ethyl hemiacetals were prepared by Link and Campbell[2] as the first derivatives of the aldehydo form of a hexuronic acid. Prior to this work on *d*-galacturonic acid Wolfrom and Morgan[3] had prepared the corresponding derivatives of the parent sugar *d*-galactose. They also reported[4,5] on the optical properties of aldehydo-*d*-galactose pentaacetate and its hemiacetals. In this communication we have extended the mutarotation and rotatory dispersion study to the aldehydo derivatives of *d*-galacturonic acid.

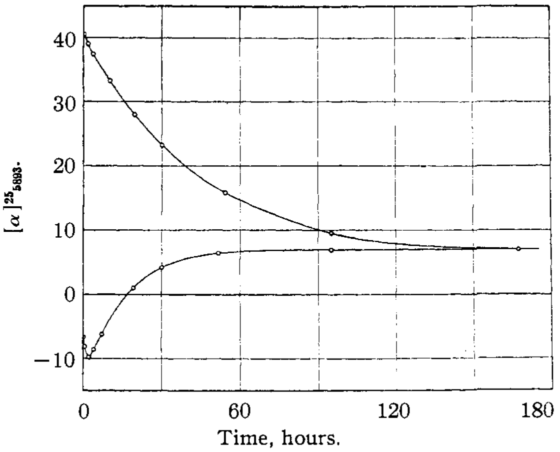
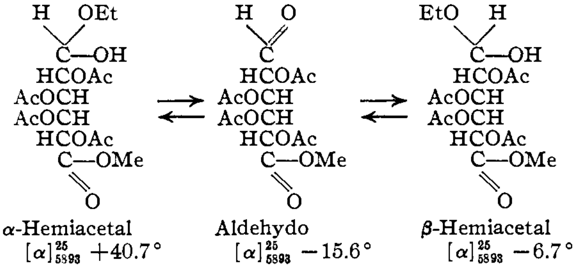


Fig. 1.—Mutarotation of α- and β-ethyl hemiacetal tetraacetyl methyl *d*-galacturonate in alcohol-free chloroform.

The isomeric α- and β-ethyl hemiacetals of tetraacetyl methyl-*d*-galacturonate have been obtained by variation of the method of preparation and fractional crystallization. This is the first member of the hemiacetal series for which both of the predictable forms have been realized. The designation of the isomers as α- and β- is based on the usage proposed by Hudson,[6] in which that derivative in the *d*-series having the more positive rotation is assigned the prefix α. The β-ethyl hemiacetal exhibits a mutarotation (Fig. 1) similar to that of the compounds of galactose studied by Wolfrom.[5] The α-ethyl hemiacetal shows a regular mutarotation without a minimum as seen in Fig. 1.

The mutarotation of the α- and β-ethyl hemiacetals involves the establishing of an equilibrium among the three compounds.



α-Hemiacetal $[\alpha]^{25}_{5893}$ +40.7° Aldehydo $[\alpha]^{25}_{5893}$ −15.6° β-Hemiacetal $[\alpha]^{25}_{5893}$ −6.7°

The minimum in the mutarotation curve for the β-ethyl hemiacetal is attributed to the primary rapid formation of the free aldehydo compound. The resulting aldehyde and alcohol recombine

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[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

This study is part of a thesis to be submitted to the Graduate Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. R. J. Dimler is indebted to the Wisconsin Alumni Research Foundation for a fellowship in 1936–37 and to the Graduate Research Fund for an assistantship in 1937–40.

[2] Campbell and Link, *J. Biol. Chem.*, **120**, 471 (1937).

[3] Wolfrom and Morgan, THIS JOURNAL, **52**, 2464 (1930).

[4] Wolfrom, *ibid.*, **53**, 2275 (1931).

[5] Wolfrom and Morgan, *ibid.*, **54**, 3390 (1932).

[6] Hudson, *ibid.*, **31**, 66 (1909).

in a second order reaction to form either of the isomeric hemiacetals. Since the concentration of the reactants in this reaction is low, the ratio of the aldehydo form will be high, as shown by the rotation of the equilibrium mixture. While differences in the *rate* of mutarotation for independent determinations can be noted, the curves obtained are of reproducible form. These variations are probably due to catalysts arising in the chloroform on standing. The nature of the compounds involved has not been investigated.[7]

The ethyl ester of ethyl hemiacetal tetraacetyl *d*-galacturonic acid, prepared in order that a compound might be used in which both alkyl groups were the same, was obtained only in the form of the β-isomer. The mutarotation, as shown in Fig. 2, is typical of the β-hemiacetals.

The rotatory dispersion of aldehydo pentaacetyl *d*-galactose was shown by Hudson, Wolfrom and Lowry[8] to be attributable to the induced dissymmetry of the aldehyde group, with only a small contribution from the other asymmetric centers of the molecule. The galacturonic acid structure contains another possible source of induced activity, namely, the carboxyl group (as the ester).

TABLE I

ROTATORY DISPERSION OF ALDEHYDO TETRAACETYL METHYL *d*-GALACTURONATE

$$[\alpha]^{25}_{\lambda} = -\frac{13.81}{\lambda^2 - 0.090} + \frac{11.12}{\lambda^2 - 0.055};\quad (c, 4;\ CHCl_3)$$

λ, Å.	$[\alpha]^{25}_{\lambda}$	O − C[a]
4358	−54.4	+1.4
4679	−39.2	±
4800	−34.9	+0.2
4861	−33.0	+0.2
5086	−27.1	+0.1
5209	−24.7	+0.1
5350	−22.3	±
5461	−20.6	+0.1
5780	−16.8	±
5893	−15.6	±
6104	−13.9	−0.1
6362	−12.0	±
6438	−11.6	±
6563	−11.0	−0.1
6708	−10.2	±

[a] O − C is the difference between the observed specific rotation and the rotation calculated from the Drude equation.

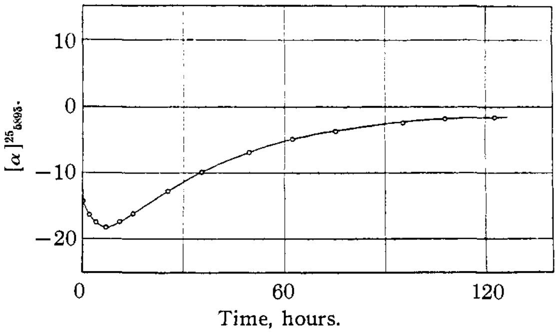

Fig. 2.—Mutarotation of β-ethyl hemiacetal tetraacetyl ethyl *d*-galacturonate in alcohol-free chloroform.

The methyl and ethyl esters of aldehydo tetraacetyl *d*-galacturonic acid were shown to have a complex rotatory dispersion by a preliminary plotting of the reciprocal of the specific rotation against the square of the wave length, the points lying on a curve instead of a straight line. Two-term Drude equations were then determined for the dispersions. These equations, with the difference between the observed rotations and those calculated from the equations, are given in Tables I and II. Since the observations were made only in the visible region of the spectrum the significance of the Drude equations is more qualitative than quantitative.

TABLE II

ROTATORY DISPERSION OF ALDEHYDO TETRAACETYL ETHYL *d*-GALACTURONATE

$$[\alpha]^{25}_{\lambda} = -\frac{12.42}{\lambda^2 - 0.090} + \frac{7.07}{\lambda^2 - 0.055};\quad (c, 4;\ CHCl_3)$$

λ, Å.	$[\alpha]^{25}_{\lambda}$	O − C[a]
4358	−71.0	+0.8
4678	−53.1	±
4800	−48.1	+0.1
4861	−45.8	+0.1
5086	−38.8	±
5209	−35.8	+0.1
5350	−32.8	−0.1
5461	−30.7	−0.1
5780	−25.5	+0.1
5893	−24.0	+0.1
6104	−21.6	±
6362	−19.2	±
6438	−18.6	±
6563	−17.5	+0.1
6708	−16.5	+0.1

[a] O − C is the difference between the observed specific rotation and the rotation calculated from the Drude equation.

The rotatory dispersion of the methyl and ethyl esters of aldehydo tetraacetyl *d*-galacturonic acid is complex but normal. The rotation is

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[7] Wolfrom[4] has suggested that hydrogen chloride is the responsible agent. We have observed that dry or moist hydrogen chloride or absolute alcohol in chloroform has no effect on the rate. However, alcoholic hydrogen chloride produces immediate equilibrium.

[8] Hudson, Wolfrom and Lowry, *J. Chem. Soc.*, 1179 (1933).

dominated by the activity due to the induced dissymmetry of the aldehyde group, with an active band at about 2900 Å. A comparison of rotation constants of the two different esters and also the galactose derivative studied by Hudson, *et al.*,[8] shows that the groups on the terminal carbon remote from the aldehyde group have little influence on the magnitude of the activity induced in the carbonyl group. This is in accord with the present conception of induced dissymmetry.

The remaining active groups contribute a rotation of opposite sign and smaller magnitude. The dispersion constant may be assigned to the induced dissymmetry of the carboxyl group, with an active absorption band in the region of 2300 Å. While the carboxyl group often shows another active band at about 1700 Å., the limited range of dispersion studied in this case does not permit consideration of the possibility of such a contribution. Similarly, the small contribution of the other asymmetric centers, demonstrated for galactose, cannot be detected in this study. It may be concluded that the dispersion is probably more complex than is implied by a two-term Drude equation. The equations obtained indicate only the dominant sources of optical activity.

Experimental

Standardization of the Polarimeter.—The rotatory dispersions were studied with the use of a Franz Schmidt and Haensch polarimeter No. 52B with a monochromator attachment. The instrument was standardized by a modification of the method of Bencowitz.[9] A spectroscope was set with a sodium light and checked against a mercury arc. This spectroscope was then used to determine the wave length of the light transmitted by the monochromator. The settings were thus determined for the monochromator which would give the desired wave lengths. The results were checked by determining the rotatory dispersion of a 26% solution of Bureau of Standards sucrose, for which the dispersion formula is known.

Ethylmercaptal Methyl-*d*-galacturonate.—The method used by Campbell and Link[2] was modified to permit simultaneous mercaptalation and esterification. To a solution of 10 g. of *d*-galacturonic acid in 60 cc. of approximately 1 *N* hydrogen chloride–methanol (dry), was added 15 cc. of ethyl mercaptan. After standing at room temperature for one and one-half hours, the solution was refluxed gently for one-half hour. Concentration of the solution under reduced pressure gave a mass of crystals which was removed by filtration and washed with cold methanol. The mother liquors were concentrated to obtain another crop of crystals. In this way about four crops of crystals were obtained; yield of the crude product was 9.2 g. (57%). For acetylation it is sufficient to dry the crude preparation in a vacuum desiccator. If the product is to be kept for any length of time it should be recrystallized since the hydrogen chloride adhering to the crystals may cause decomposition.

Ethylmercaptal Tetraacetyl Methyl-*d*-galacturonate.—The method used was that described by Campbell and Link.[2] From the 9.2 g. of ethylmercaptal methyl-*d*-galacturonate prepared as above about 11.5 g. (71%) of the acetate (recrystallized once, m. p. 109–110°) was obtained.

Aldehydo Tetraacetyl Methyl-*d*-galacturonate.—This compound was prepared by the method of Wolfrom and Morgan.[3] The crude product was recrystallized several times to obtain the pure aldehydo tetraacetyl methyl-*d*-galacturonate; m. p. 135–136°; $[\alpha]^{25}_{5893}$ −15.6° (*c*, 4; $CHCl_3$).

The rotatory dispersion in alcohol-free chloroform was determined in a 4-dm. semi-micro jacketed tube at 25°. The rotations obtained with a comparison to the values calculated from the two-term Drude equation, are given in Table I.

Anal. Calcd. for $C_{15}H_{20}O_{11}$: $-OCH_3$, 8.25. Found: $-OCH_3$, 8.29.

β-Ethylhemiacetal Tetraacetyl Methyl-*d*-galacturonate.—Without fractionation the first time, 2.5 g. of the crude aldehydo compound was crystallized from 8 cc. of boiling absolute ethanol. The resulting 1.8 g. of crude ethyl hemiacetal was recrystallized with fractionation from 8 cc. of boiling ethanol. The first crop obtained from quiescent crystallization was 0.8 g.; initial $[\alpha]^{25}_{5893}$ −5.9°. The second crop, obtained by vigorous stirring of the mother liquor, was 0.2 g.; initial $[\alpha]^{25}_{5893}$ +3.0°. Repeated fractional crystallizations of the first fractions yielded the apparently pure β-isomer; m. p. 127–130° (on the Kofler microscope stage[10] with crossed nicols one observes the loss of ethyl alcohol at about 127° and the sharp melting of the remaining aldehydo compound at 135–136°); $[\alpha]^{25}_{5893}$ −6.7° initial, with equilibrium value of +7.1° (*c*, 4; $CHCl_3$).

The mutarotation of the ethyl hemiacetal in alcohol-free chloroform is shown by the curve in Fig. 1. Independent determinations showed differences in the length of time required to reach equilibrium, but the form of the curve was the same for all. The differences in rate probably are due to catalysts formed in the chloroform on standing.

Anal. Calcd. for $C_{17}H_{26}O_{12}$: alkoxyl, 18.06. Found: alkoxyl, 18.2.

α-Ethyl Hemiacetal Tetraacetyl Methyl-*d*-galacturonate.—The ethyl hemiacetal was prepared directly from the mercaptal by the method of Campbell and Link.[2] The 5.3 g. of crude product was recrystallized first without fractionation from absolute alcohol. On fractional crystallization of the 3.7 g. from 10 cc. of boiling absolute alcohol, as above, the first crop was 0.5 g., initial $[\alpha]^{25}_{5893}$ −2.2°; the second crop was 2.1 g., initial $[\alpha]^{25}_{5893}$ +15.8°. Further fractionation of second crops yielded the apparently pure α-isomer; m. p. 105–107° (on the Kofler microscope stage loss of ethyl alcohol is observed at about 105° and melting of the aldehydo compound at 135–

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[9] Bencowitz, *J. Phys. Chem.*, **32**, 1163 (1928).

[10] Pregl–Roth, "Die quantitative organische Mikroanalyse," Berlin, 1935.

136°); $[\alpha]^{25}_{5893}$ +40.7° initial, changing to a final value of +7.1° (*c*, 4; $CHCl_3$).

The mutarotation, observed in alcohol-free chloroform, is shown by the curve in Fig. 1.

Anal. Calcd. for $C_{17}H_{26}O_{12}$: alkoxyl, 18.06. Found: alkoxyl, 18.1.

Ethylmercaptal Ethyl-*d*-galacturonate.—This compound was prepared from *d*-galacturonic acid in the same manner as the methyl ester. A dry hydrogen chloride–ethanol solution (approx. 1 *N*) was used as the solvent. The ethyl ester did not crystallize as readily as the methyl ester. By the repeated addition of absolute ethanol and removal under reduced pressure crystallization was induced. The concentrate was placed in a refrigerator for twenty-four hours to permit more complete crystallization.

From 10 g. of *d*-galacturonic acid, the yield was 9.6 g. (57%). Recrystallization from absolute ethanol gave a pure product; m. p. 128–129°; $[\alpha]^{25}_{5893}$ +15.7° (*c*, 2; EtOH).

Anal. Calcd. for $C_{12}H_{24}O_6S_2$: S, 19.53. Found: S, 19.62.

Ethylmercaptal Tetraacetyl Ethyl-*d*-galacturonate.—This acetyl derivative was prepared by the same method used for the corresponding methyl ester. From 9.6 g. of crude ethyl mercaptal ethyl ester the yield after one recrystallization was 11.5 g. (79%); m. p. 80–81°; $[\alpha]^{25}_{5893}$ +11.0° (*c*, 4; $CHCl_3$).

Anal. Calcd. for $C_{20}H_{32}O_{10}S_2$: S, 12.92. Found: S, 12.93.

Aldehydo Tetraacetyl Ethyl-*d*-galacturonate.—The preparation is similar to that of the corresponding methyl ester. The compound is quite soluble in toluene; m. p. 95–97°; $[\alpha]^{25}_{5893}$ −24.0° (*c*, 4; $CHCl_3$).

The rotations obtained in the study of the rotatory dispersion with a comparison to the values calculated from the two-term Drude equation, are given in Table II.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: —OEt, 11.54. Found: —OEt, 11.7.

β-Ethylhemiacetal Tetraacetyl Ethyl-*d*-galacturonate.—The hemiacetal was prepared by both of the methods which were used for the methyl ester. The resulting compounds were apparently identical and could not be fractionated; m. p. 105–106°; $[\alpha]^{25}_{5893}$ −14.4° initial, reaching equilibrium at −1.6° (*c*, 4; $CHCl_3$). The course of the mutarotation, observed in alcohol-free chloroform, is shown by the curve in Fig. 2.

Anal. Calcd. for $C_{18}H_{28}O_{12}$: —OEt, 20.70. Found: —OEt, 20.8.

Summary

1. The α- and β-ethyl hemiacetals of aldehydo tetraacetyl methyl-*d*-galacturonate have been prepared. The mutarotation of the two compounds in chloroform indicates an interconversion over the aldehydo form.

2. The ethyl ester of ethyl mercaptal, ethyl mercaptal tetraacetyl, aldehydo tetraacetyl and ethyl hemiacetal tetraacetyl *d*-galacturonic acid have been prepared. Through mutarotation studies the ethyl hemiacetal tetraacetyl ethyl-*d*-galacturonate obtained is characterized as a β-hemiacetal.

3. The rotatory dispersions of the aldehydo tetraacetyl methyl- and ethyl-*d*-galacturonate have been shown to be complex but normal. Two-term Drude equations have been calculated for the dispersions to obtain a qualitative interpretation of the results.

MADISON, WISCONSIN RECEIVED MARCH 1, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of Certain Compounds of Sulfur, Selenium and Phosphorus

BY C. P. SMYTH, G. L. LEWIS, A. J. GROSSMAN AND F. B. JENNINGS, III

The dipole moments of hydrogen disulfide and sulfur and selenium monochlorides have been measured with a view to obtaining evidence as to the two possible structures, the Y-shaped or irregular tetrahedral such as $S—SCl_2$ and the more extended structures such as Cl—S—S—Cl, as well as getting some information bearing on the magnitudes of the bond moments. Selenium oxychloride and phosphoryl and thiophosphoryl chlorides have been investigated for the sake of the bond moments involved. Indeed, bond moment values obtained from the measurements on the two latter compounds already have been published,[1] and electron diffraction measurements have been made upon the more volatile of these several substances. The moments were obtained with the apparatus and methods previously described,[2,3] the dielectric constants and densities of solutions of the substances in benzene or heptane being determined.

Preparation of Materials.—Benzene and heptane were purified as in previous work.[4]

Hydrogen Disulfide.—The material was prepared from sodium polysulfide and purified in the manner described

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[1] Smyth, THIS JOURNAL, **60**, 183 (1938).

[2] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[3] Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

[4] Smyth and Walls, *ibid.*, **54**, 1854 (1932).