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Degradation of Methyl α-D-*gluco*-Hexodialdopyranoside-(1,5) in Aqueous Solution

HÅKAN F. G. BEVING and OLOF THEANDER

Swedish Forest Products Research Laboratory, Chemistry Department,
Box 5604, S-114 86 Stockholm, Sweden

The degradation of methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (I) *via* β-elimination to methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5) (II) at various temperatures in aqueous alkali and the further degradation of II in the pH range 1.2 – 12.5 was studied. At low pH values, 2,5-furan-dicarboxaldehyde (III) and 4-*H*-pyran-2-carboxaldehyde-4-one (IV) are formed. The relevance of the result to the yellowing of oxidized cellulose is discussed.

Cellulose products are degraded under the influence of air and light. The degradation, particularly of the hemicellulose polysaccharides, causes yellowing which is accelerated at elevated temperatures. In a previous investigation in this laboratory concerning the formation of aromatic compounds from carbohydrates, reductic acid, furan and benzene derivatives were isolated after treatment of pentoses and uronic acids in slightly acidic solutions.[1] These compounds are precursors of chromophoric products. In another investigation it was shown that the presence of even a small number of 6-aldehydo groups in cellulose resulted in rapid depolymerisation and extensive colour formation during dry or humid aging.[2] Introduction of 6-aldehydo groups into cellulose material is a possible reaction among other oxidative modifications from bleaching and/or through oxidation during storage and use of the material.

Methyl 6-aldehydo-D-glycopyranosides and methyl 6,6′-dialdehydo-β-D-cellobioside have been used as model compounds for celluloses specifically oxidized at the 6-position.[3–5] When these substances are treated at different pH values, elimination at C-4 is the primary reaction from pH 4 and upwards. This leads to 4,5-unsaturated glycosides. The rate of this degradation becomes more important at increasing pH values (*cf.* uronate degradation [6]). At low pH values pure acid hydrolysis is the main reaction.

In our continued efforts at obtaining an understanding of the processes responsible for the yellowing of cellulose we now report on the degradation of methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (I). The degradation of isomers of hexodialdopyranoside-(1,5) at various pH values has recently been studied.[3] Elimination, leading to hex-4-eno-dialdohexopyranosides is the predominant reaction above pH 4.

The rate of degradation of the title compound (I) in 0.1 % aqueous potassium hydroxide (pH 12.5) to produce methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5) (II), at 50, 70, and 90 °C was studied by following the change in intensity of the absorption band at 253 nm for II and also by TLC examination of the reaction mixture. The results are shown in Fig. 1. At the higher temperature a maximum yield of II was obtained after 10 min. Further treatment caused degradation of II. At 50 °C the degradation of I was slow, significant amounts of starting material remaining after 70 min. Treatment of I at 70 °C, however, left no starting material after 40 min, and II was obtained in a 90 % yield. The substance II was stable in aqueous solution at 4 °C for several weeks. The formation of II was found to follow

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* Present address: Department of Chemistry, Div. II, Agricultural College of Sweden, S-750 07 Uppsala, Sweden.

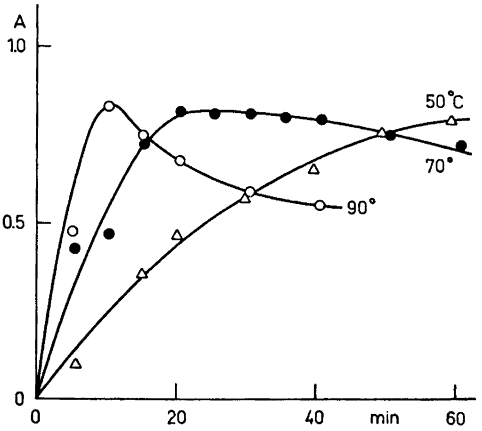


Fig. 1. Variation in UV absorbance at 253 nm during treatment of methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (I) in aqueous alkaline solution (pH 12.5) a various temperatures.

first-order kinetics. The rate constants were found to be 754×10^{-6} s^{-1} at 50 °C and 3270×10^{-6} s^{-1} at 70 °C at pH 12.5. Although compound I was only present in concentrations of 0.3 mM in these experiments, a distinct yellowing was apparent, indicating a high molar extinction for the coloured products. This strongly emphasizes the importance of 6-aldehydoglucose units in the yellowing of oxidized cellulose materials.

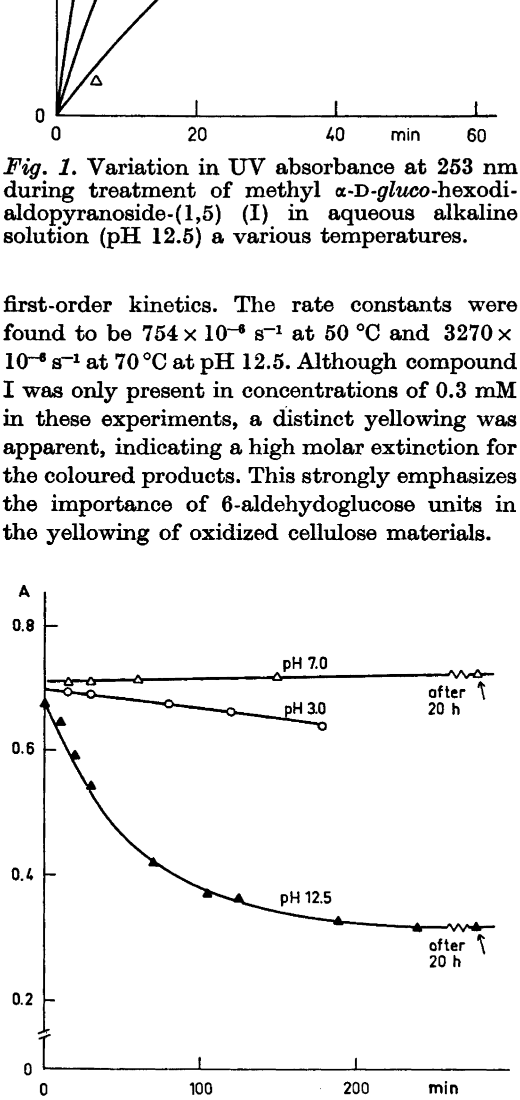


Fig. 2. Decrease in UV absorbance at 253 nm during treatment of methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside(1,5) (II) at different pH-values at 80 °C.

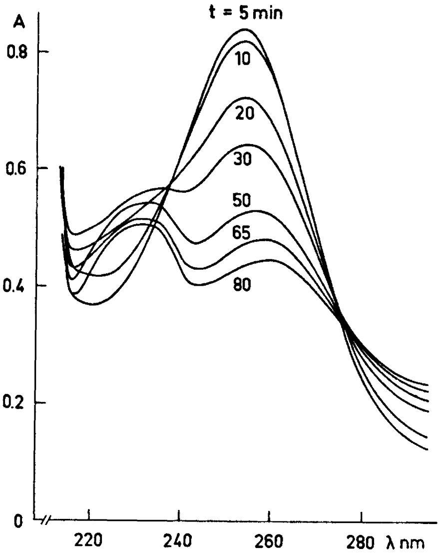


Fig. 3. UV spectra for the degradation of methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5) (II) in aqueous alkaline solution (pH 12.5) at 80 °C.

The rate of degradation of II at pH 3.0, 7.0, and 12.5 and 80 °C was followed by observing the decrease of the absorption band at λ_{max} 253 nm (Fig. 2). The processes followed first-order kinetics and gave rate constants of 13.2×10^{-6}, ~ 0 and 326×10^{-6} s^{-1}, respectively (compare the rate of I→II at 70 °C 3270×10^{-6} s^{-1}). A yellow colour appeared at an early stage. The UV spectra for the degradation of II at the higher pH value are shown in Fig. 3. These results show that the unsaturated 6-aldehydoglycoside II has a maximum stability at pH 7 or slightly below and is degraded much more slowly at alkaline pH than is the parent substance I.

In previous investigations [3,4] it was found that the elimination reaction of methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (I) and other 6-aldehydo-glycopyranosides operated already at acid pH values forming the corresponding unsaturated glycosides. On the other hand reductic acid, 2-furaldehyde, chromones, and cathecols, all active precursors of chromophoric products, were isolated after acid treatment of pentoses and uronic acids.[1] It was therefore of interest to examine the degradation products from II after acid treatment (at pH 12.5 no low-molecular products were detectable).

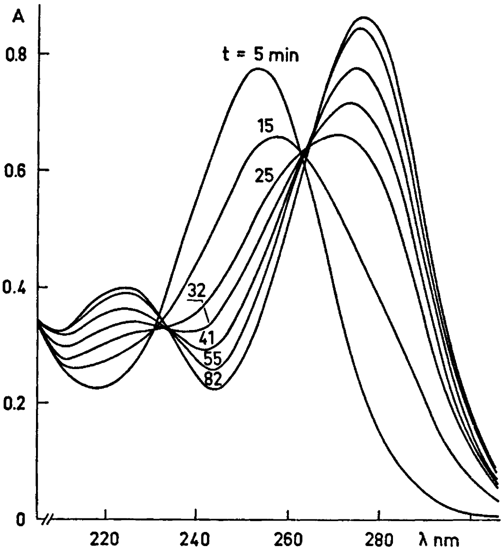
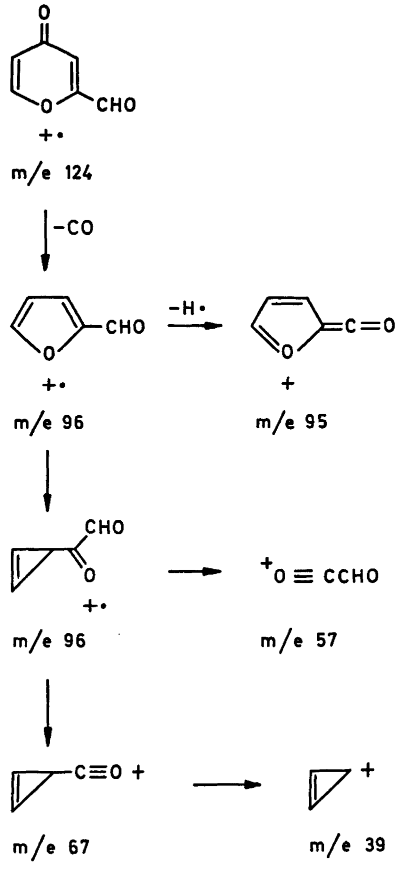


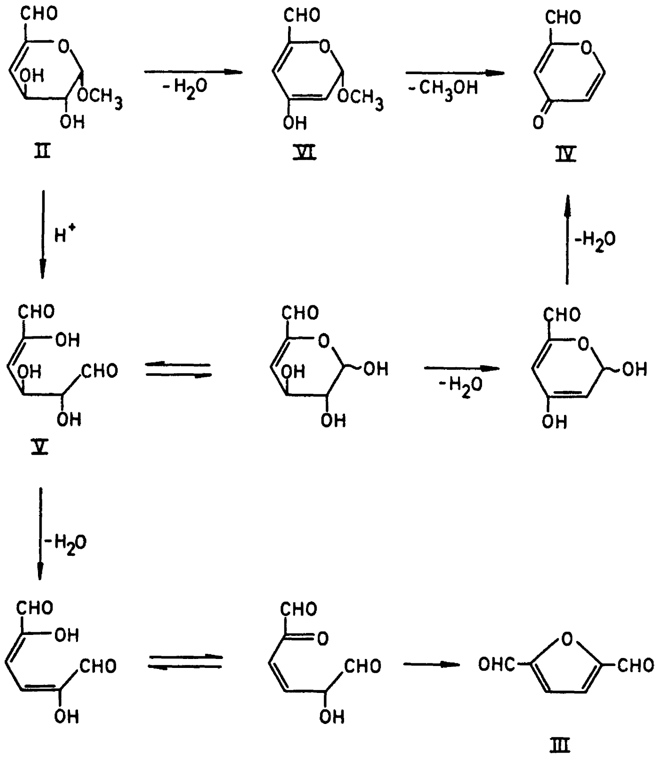
Fig. 4. UV spectra for the degradation of methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5) (II) in aqueous hydrochloric acid (pH 1.2) at 80 °C.



Scheme 1.

For the purpose of studying the formation of chromophoric compounds, II was treated at pH 1.2 and 80 °C. The change with time of the UV spectrum for this process is shown in Fig. 4. The degradation of II obviously is rapid, but kinetic studies using the absorption band λ_{max} 253 nm were not possible. The degradation was followed by TLC which showed the presence of one minor and two more predominant reaction products (III and IV); the two latter were carbonyl compounds, as indicated by strong positive reaction with the spray reagents 2,4-dinitrophenylhydrazine and anisidine hydrochloride. The two compounds were obtained by TLC on the mixture produced by the acidic degradation of II. III was obtained in crystalline form in a yield of 0.4 % and was found to be indistinguishable from an authentic sample of 2,5-furan-dicarboxaldehyde[7] (m.p., mixed m.p., NMR). IV was obtained as an unstable syrup in 1 % yield. By comparison of the spectrum to that of 4-*H*-pyran-4-one-2-carboxylic acid methyl ester[8] (methyl comanate) and by analysis of its mass fragmentation, IV was identified as 4-*H*-pyran-2-carboxaldehyde-4-one which, to the best of our knowledge, is a new substance. A possible rationalization of its fragmentation on MS is outlined in Scheme 1; the MS is analogous to spectra of γ-pyrones reported by Nakata and Tatematsu.[9] Possible pathways for the formation of III and IV from the unsaturated aldehyde II are outlined in Scheme 2.

The formation of III may pass *via* hydrolysis of the glycosidic linkage to the unsaturated dialdose V which is then reacting in a similar way as the formation of 5-(hydroxymethyl)-2-furaldehyde from hexoses[10] (Scheme 2). IV may also be formed from the same acyclic intermediate (V), but a route without ring opening *via* VI is also possible. The latter route is supported by recent results on acid treatment of the 2,3-dimethyl ether of II which yielded III and unchanged dimethyl ether of II.[11,12] It was found that the rate of acid hydrolysis of



Scheme 2.

the glycoside II was of the same order as the rate of degradation of II to III.

The above results indicate that the compounds III and IV are possible precursors of chromophoric products in the acid degradation of celluloses containing aldehydo groups in the 6-position of the anhydroglucose units.

EXPERIMENTAL

Melting points are corrected. Concentrations were perforned at reduced pressure below 40 °C unless otherwise stated.

TLC was performed on silica gel HF_{254} (Merck) plates with (a) water-saturated butanone, (b) ethyl acetate-methanol 4:1, and (c) ethyl acetate-cyclohexane 1:1. For preparative TLC 0.5 mm thick layers on 20 x 20 cm plates were used. Zones were detected with UV light. Standard spray reagents were used for sugars, carbonyl compounds and phenols (or enols), namely (a) *p*-anisidine hydrochloride, (b) resorcinol-hydrochloric acid, (c) silver nitrate-sodium hydroxide, (d) 2,4-dinitrophenyl hydrazine, (e) diazotized sulfanilic acid, and (g) ferric chloride. Spots on TLC plates were also studied in UV light (254 nm and 366 nm) before spraying. Products that were unreactive towards the above reagents were detected with 50 % aqueous sulfuric acid (and heating) or with iodine vapour.

UV measurements were carried out on Beckman DK 2 and Zeiss PMQ II spectrometers. IR spectra were obtained with a Perkin-Elmer 337 spectrometer. NMR measurements were carried out with a Perkin-Elmer R-12 60 MHz spectrometer using tetramethylsilane as an internal reference. Mass spectrometry was performed on a Perkin-Elmer 270 spectrometer with ionisation voltage 70 eV and ion current 80 μA.

Kinetic experiments. A sample of I or II (50 mg) was dissolved in water to 100 ml. 1 ml of this solution was added to aqueous buffer solution (50 ml). Experiments were conducted in 0.1 mol/l aqueous buffers: pH 1.2, hydrochloric acid; pH 3.0, potassium formate; pH 7, potassium phosphate, and pH 12.5, potassium hydroxide. The solutions also contained 0.1 mol/l potassium chloride. The solutions were kept in stoppered glass flasks placed in a constant temperature bath of 50, 70, 80 or 90 °C. At time intervals, aliquots (4 ml) were removed, cooled and the absorbance at λ_{max} 253 nm was measured. Plots of absorbance as a function of time are shown in Figs. 1 and 2. The reactions were studied over three halflifes in each case. The reaction spectra for degradation of II at 80 °C are shown in Figs. 3 and 4 for pH 12.5 and pH 1.2, respectively. The pseudo-first-order rate constants[13] were calculated from plots of log $[(A_\infty - A_0)/(A_\infty - A_t)]$ *versus* time according to eqn. (1).

$$k = \frac{2.303}{t_2 - t_1}\left[\log\frac{A_\infty - A_0}{A_\infty - A_{t_2}} - \log\frac{A_\infty - A_0}{A_\infty - A_{t_1}}\right] \qquad (1)$$

*Methyl 4-deoxy-β-*L-threo-*hex-4-enodialdo-pyranoside-(1,5) (II).* Methyl α-D-*gluco*-hexodialdopyranoside-(1,5)[14] (I) (7.0 g) was dissolved in 0.05 M potassium hydroxide (700 ml). The solution was heated at 70 °C for 40 min, cooled in ice-water and neutralized to pH 6 with Dowex 50 (H+). The solution was concentrated below 40 °C and stored at 4 °C. TLC (solvent a) revealed small amounts of polymeric substance together with II (R_F 0.65), and no other reaction products were detected. The yield obtained by preparative TLC was *ca.* 90 %. The optical rotation and UV data were in accordance with those of an authentic sample.[3] Samples from the aqueous solution of II were used for the kinetic experiments without prior evaporation of the solvent as II was unstable in the solid state.

*2,5-Furan-dicarboxaldehyde (III)[7] and 4-*H*-pyran-2-carboxaldehyde-4-one (IV) from acid degradation of II.* A sample (210 ml) of the stock solution containing II (3.5 g) was acidified with 1 M sulfuric acid to pH 1.0. The solution was kept at 80 °C for 100 min. At time intervals, aliquots (4 ml) were removed, diluted with water and the UV absorbtion spectra were recorded. The reaction spectrum was similar to that obtained at pH 1.2 (Fig. 4).

TLC analysis showed that almost all starting material, R_F 0.62 (solvent b), had reacted and two new substances, R_F 0.51 (III) and R_F 0.75 (IV), had been formed. In solvent c, however, three new compounds with R_F values 0.30 (III), 0.43 (IV), and 0.62 (minor), respectively, appeared (together with polymeric material).

All of these three compounds were visible in short wave UV light on the TLC plates. The first component with R_F 0.62 gave a faint blue colour with *p*-anisidine spray followed by sulfuric acid spray (after 1 – 2 days) and was not further characterized. III gave a strong red colour whereas IV gave a yellow colour with these spray reagents.

Extraction of the reaction mixture with methylene chloride and evaporation of the organic phase yielded a syrup (200 mg). Compounds III and IV were isolated after separation by preparative TLC with methylene chloride. The plates were developed three times in the solvent. Elution of the preparative plates with methylene chloride gave crystalline III (11 mg, 0.44 %), m.p. 108 – 110 °C. Cooper and Nuttall[7] give m.p. 109.5 – 110 °C. III had λ_{max} (EtOH) 281 nm, ε 11 550. NMR ($CDCl_3$): δ 7.25 (2 H, s, H-3 and H-4), 9.85 (2 H, s, CHO). The chromatographical and NMR data of III were identical with those of an authentic sample of 2,5-furan-dicarboxaldehyde.

IV was obtained as a viscous syrup (30 mg, 1.2 %). By storing at room temperature it was degraded to coloured polymeric material and a small amount of a compound with higher R_F value. This degradation product was visible in short wave UV light but did not react with *p*-anisidine spray. After a week at room temperature IV was completely degraded. No attemps were made to isolate the degradation products. IV showed the following spectra data $\lambda_{max}(CH_2Cl_2)$ 272 nm, ε 11 100; ν_{max} (KBr) 1705 cm^{-1} (CHO) and 1620 cm^{-1} (γ-pyrone C=O); NMR ($CDCl_3$): δ 6.62 (1 H, dd, $J_{3,5}$ 2.7 Hz, $J_{5,6}$ 5.6 Hz, H-5), 7.30 (1 H, broad s, H-3), 7.72 (1 H, broad s, H-6) and 9.68 (1 H, s, CHO). These NMR data are similar to those given by Elvidge and Stevens[8] for 4-*H*-pyran-4-one-2-carboxylic acid methyl ester (methyl comanate). Mass spectrum: *m/e* 39 (66 %), 57(6), 67(14), 95(95), 96(100), 124(4,M+), as significant fragments of a γ-pyrone structure.[9] These data identified IV as 4-*H*-pyran-2-carboxaldehyde-4-one.

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