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The Oxidation of Glycosides. XVIII.* Effect of pH on the Degradation of Various Isomers of Methyl Hexodialdopyranoside-(1,5)

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The degradation of various isomers of methyl hexodialdopyranoside-(1,5) with the α-D-*galacto* (I), α-D-*gluco* (II), β-D-*gluco* (III). the 4-*O*-methyl ether of III (IV), α-D-*gulo* (V), β-D-*gulo* (VI) and α-L-*manno* (VII) configurations have been investigated at 90 °C and pH 1.5 – 6. A minimum rate in the oxidation was observed at pH 3 – 4. Below this range acid hydrolysis of the glycosidic linkage predominated and above this range β-elimination. The products of β-elimination were detected at pH values, as low as 4. Partial isomerization of the two D-*gulo* derivatives V and VI to the corresponding L-*manno* derivatives *via* C-5 epimerization at pH 4 – 6 was observed.

The rate of alkaline degradation of II has been determined at 23 °C in aqueous sodium and calcium hydroxide.

Methyl β-D-*arabino*-hexopyranosid-2-ulose, methyl β-D-*ribo*-hexopyranosid-3-ulose and methyl β-D-*gluco*-hexodialdopyranoside-(1,5) are formed when methyl β-D-glucopyranoside is treated with chlorine water or other oxidizing agents and these substances have been investigated as models for oxidized cellulose.[1] Carbonyl groups at position 2 or 3 make the glycoside units more labile in acid and alkaline media than the corresponding unoxidized units.[2,3] Methyl β-D-*arabino*-hexopyranosid-2-ulose and methyl β-D-*ribo*-hexopyranosid-3-ulose give dark coloured reaction mixtures when treated with aqueous acid or alkaline solution. In acid solution, reductic acid is the main reaction product whereas in alkaline solution 1,5-anhydro-D-*erythro*-2,3-hexodiulose is formed rapidly by β-elimination and is further degraded to acids. Hydrolysis of methyl β-D-*gluco*-hexodialdopyranoside-(1,5) (III) in aqueous sulfuric acid gives almost exlusively D-*gluco*-hexodialdose.[4,5]

In the present paper we report the results of studies on the degradation of isomers of methyl hexodialdopyranoside-(1,5) with the α-D-*galacto* (I), α-D-*gluco* (II), β-D-*gluco* (III), the 4-*O*-methyl ether of III (IV), α-D-*gulo* (V), β-D-*gulo* (VI) and α-L-*manno* (VII) configuration at 90 °C and pH 1.5 – 6. The rate of degradation of IV was also determined in aqueous sodium and calcium hydroxide at 23 °C and pH 11.5.

The syntheses of I, V, VI, and VII have previously been communicated from this laboratory;[6] Horton *et al.*[7] have reported the synthesis of II. The remaining substances, III and V, were prepared by photolysis of the appropriate 6-azido glycosides by the method devised by Horton *et al.*[7]

The 6-aldehydo glycosides (I – VII) were kept in buffered solutions at 90 °C. L-Rhamnitol was present as internal standard.

Samples were withdrawn at intervals, reduced, acetylated and analyzed by GLC. The rate constants for the degradations were calculated, assuming first-order kinetics. The regression in the lines obtained were in agreement with this assumption except for the two D-*gulo* derivatives V and VI. The rate *versus* pH of com-

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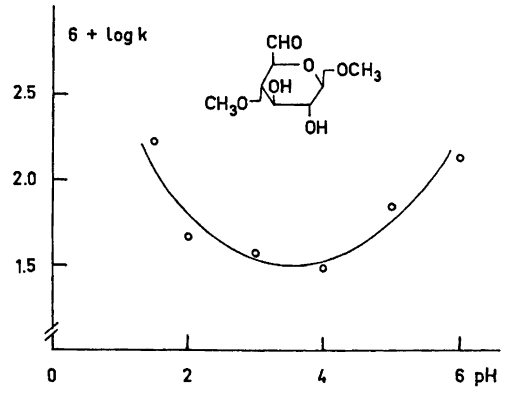


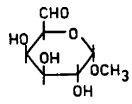
Fig. 1. Degradation of methyl 4-*O*-methyl-β-D-*gluco*-hexodialdopyranoside-(1,5) (IV) at 90 °C in the pH range 1.5 – 6.

pound IV is shown in Fig. 1. The rates of degradation are lowest at pH 3 – 4 (Table 1). At low pH values, the degradation is essentially due to acid hydrolysis of the glycosidic linkage and the corresponding hexitol acetates were observed on GLC of the reduced, acetylated product. At higher pH values, the degradation is essentially due to elimination of the substituent at C-4; the isomers of methyl 4-deoxy-hex-4-enopyranoside-(1,5) thus formed were detected by the strong absorption at 253 nm.[8,9] The formation of these products at pH values as low as 4 was demonstrated. The maximum stability of the methyl 6-aldehydo-glycopyranosides at this pH-range is in accordance with the maximal yield of methyl β-D-*gluco*-hexodialdopyranoside-(1,5) from the chlorine/hypochlorite oxidation of methyl β-D-glucopyranoside at pH 4.[10]

Methyl 4-deoxy-β- and α-L-*threo*-hex-4-enodialdopyranoside-(1,5) (XI and XII, respectively) were also isolated after degradation of II and III at pH 6 and 90 °C for 24 h and transferred into the diacetates, both of which were indistinguishable (NMR, UV) from authentic samples. In addition, the unsaturated aldehyde XI on borohydride reduction afforded methyl 4-deoxy-β-L-*threo*-hex-4-enopyranoside. The influence of 4-*O*-methyl substitution on the rate of acid hydrolysis has been discussed previously.[4] The influence of the size of the group at C-4 on the rate of β-elimination has been noted in earlier studies on monosaccharide derivatives and oligosaccharides.[11] Compound IV was degraded faster than III over the whole

Table 1. Rate constants for the degradation of the isomers of methyl hexodialdopyranoside-(1,5) (I – VII) in buffer solutions at 90 °C.

Compound	$k \times 10^6$ s^{-1} pH 1.5 chloride	pH 2 chloride	pH 3 phthalate	pH 4 acetate	pH 5 acetate	pH 6 phosphate
Methyl α-D-*galacto*-hexodialdo-pyranoside-(1,5) (I)	–	127	–	22	94	119
Methyl α-D-*gluco*-hexodialdo-pyranoside-(1,5) (II)	–	13	5	7	7	22
Methyl β-D-*gluco*-hexodialdo-pyranoside-(1,5) (III)	75	17	7	22	34	32
Methyl 4-*O*-methyl-β-D-*gluco*-hexodialdo-pyranoside-(1,5) (IV)	169	47	38	31	71	138
Methyl α-D-*gulo*-hexodialdo-pyranoside-(1,5) (V)	–	15	–	36	52	80
Methyl β-D-*gulo*-hexodialdo-pyranoside-(1,5) (VI)	–	27	23	17	31	28
Methyl α-L-*manno*-hexodialdo-pyranoside-(1,5) (VII)	–	44	–	21	39	45



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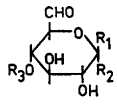
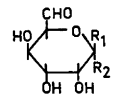
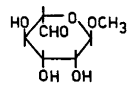


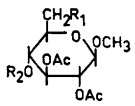
II $R_1 = R_3 = H$; $R_2 = OCH_3$
III $R_1 = OCH_3$; $R_2 = R_3 = H$
IV $R_1 = OCH_3$; $R_2 = H$; $R_3 = CH_3$



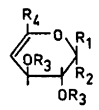
V $R_1 = H$; $R_2 = OCH_3$
VI $R_1 = OCH_3$; $R_2 = H$



VII



VIII $R_1 = N_3$; $R_2 = Ac$
IX $R_1 = Cl$; $R_2 = CH_3$
X $R_1 = N_3$; $R_2 = CH_3$



XI $R_1 = H$; $R_2 = OCH_3$; $R_3 = H$; $R_4 = CHO$
XII $R_1 = OCH_3$; $R_2 = H$; $R_3 = H$; $R_4 = CHO$
XIII $R_1 = H$; $R_2 = OCH_3$; $R_3 = Ac$; $R_4 = CHO$
XIV $R_1 = OCH_3$; $R_2 = H$; $R_3 = Ac$; $R_4 = CHO$
XV $R_1 = H$; $R_2 = OCH_3$; $R_3 = H$; $R_4 = CH_2OH$

pH-range investigated and not only by pure acid hydrolysis as previously found. The L-*manno*-isomer (VII) was degraded at a similar rate as II and III but the D-*galacto* isomer (I) was degraded faster than the corresponding D-*gluco* derivative (II) at all pH-values.

In addition to the above degradation, epimerization of the two aldehydes with the D-*gulo* configuration (V and VI) was observed at pH 4 – 6, being most pronounced at the higher pH value. The epimerized products were first observed by GLC and yielded mannose on borohydride reduction and hydrolysis, thus confirming their structure. Similar epimerizations were not observed for the other 6-aldehydoglycosides studied, probably because they, in contradistinction to the *gulo* compounds, represent the most stable C-5 epimer. In the degradation of the *gulo* derivative (as well as for the other isomers studied), only the decrease of starting materials was determined and the rate constants are, because of the epimerization, therefore not directly comparable with those for the other aldehydoglycosides. Also the degradations of the *gulo* derivatives, contrary to the derivatives of the other isomers, showed some deviation from first-order kinetics.

Table 2. Rate constants for the degradation of methyl 4-*O*-methyl-β-D-*gluco*-hexodialdopyranoside-(1,5) (IV) in aqueous alkaline solution at 23 °C.

Alkali	$k \times 10^6$ s^{-1}
0.02 M NaOH	451
0.01 M $Ca(OH)_2$	363

Methyl 4-*O*-methyl-β-D-*ribo*-hexopyranosid-3-ulose is degraded *via* β-elimination in aqueous solution chiefly at C-4 but also to a certain extent at C-1.[1] To compare the rate of alkaline degradation of methyl 4-*O*-methyl-β-D-*gluco*-hexodialdopyranoside-(1,5) (IV) and methyl 4-*O*-methyl-β-D-*ribo*-hexopyranosid-3-ulose (model compounds for oxidised cellulose), IV was treated in aqueous solution at room temperature. The degradation of IV was very rapid (Table 2) and the rates are of similar order as those obtained for IV in 0.5 M sulfuric acid at 80 °C.[4] Degradation in sodium hydroxide was faster than in calcium hydroxide. Methyl 4-*O*-methyl-β-D-*ribo*-hexopyranosid-3-ulose is degraded approximately 10 times faster than IV in 0.02 M sodium hydroxide at 25 °C.[12]

The data obtained in this investigation support the results from studies on methyl 6,6'-dialdehydo-β-D-cellobioside [13] and 6-aldehydocelluloses.[9] Steric and electronic factors certainly influence the rates at which the various aldehydoglycosides are degraded. Below pH 3 – 4 hydrolysis of the glycosidic bond seems to be the main reaction in which 3,6-hemiacetal formation may increase the rate. Above this pH-range β-elimination at C-4 and formation of methyl 4,5-unsaturated 6-aldehydo-glycopyranoside structures seem to be of increasing importance with increasing pH.

Studies on the further degradation of the methyl 4,5-unsaturated α-D-*gluco*-hexodialdopyranoside-(1,5) (VIII) will be published separately.[14]

EXPERIMENTAL

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

The irradiation used was unfiltered light from a Hanovia RCR Photochemical Reactor with a medium pressure mercury lamp of 100 W

inserted into a water cooled quartz immersion well.

Paper chromatography was performed on Whatman No. 1 paper. Solvent systems for paper chromatography were (a) ethyl acetate-acetic acid-water 3:1:1 and (b) butanol-ethanol-water 10:3:5.

Thin layer chromatography (TLC) was performed on silica gel GF_{254} (Merck, Darmstadt). Solvent systems for TLC were (a) ethyl acetate-light petroleum (b.p. 60–71 °C) 3:1, (b) ethyl acetate-methanol 4:1, (c) water saturated butanone, (d) propanol-water 85:15. Distilled solvents were used for TLC and paper chromatography.

Paper electrophoresis was run at 40 °C in (a) glycerol-boric acid buffer [15] (0.4 M boric acid, 0.1 M glycerol and 0.096 M NaOH) of pH 6.8 at 1500 V for 2 h and in (b) sodium hydrogen sulfite,[16] pH 4.7, at 1200 V for 1.5 h.

Standard spray reagents were used for sugars, carbonyl compounds, alditols and methyl glycosides namely silver nitrate-sodium hydroxide, *p*-anisidine hydrochloride, resorcinol-hydrochloric acid, periodate-benzidine. The paper chromatograms and TLC plates were studied in UV light (254 nm and 366 nm) before treatment with spray reagents. Acetates and products that were unreactive towards the above reagents were detected on TLC plates with iodine vapour.

GLC was performed on a Perkin-Elmer 801 chromatograph with a single glass column (3 % ECNSS-M on Gas-Chrom Q 100/120 mesh) and flame ionization detector. Peak areas were evaluated with an Infotronics electronic integrator. Optical rotations were measured at room temperature with a Perkin-Elmer 141 polarimeter. UV spectra were recorded on a Zeiss PMQ 2 spectrophotometer. IR spectra were obtained from a Perkin-Elmer 337 spectrometer. NMR measurements were carried out on a Perkin-Elmer R-12 60 MHz spectrometer using tetramethylsilane as internal reference. Mass spectra were recorded on a Perkin Elmer 270 mass spectrometer.

Kinetic experiments

The standard buffer solutions used were prepared as described by Gomori.[17] The degradation experiments were conducted at 90 °C in buffer solution with pH-values ranging from 1.5 to 6 or at 23 °C in aqueous alkaline solution. L-Rhamnitol was used as an internal standard and the extent of degradation was determined *via* GLC on reduced and acetylated aliquots from the reaction mixture. The quotient between the area for the acetylated methyl glycopyranoside (A) and the area for L-rhamnitol acetate (B) was calculated. Log A/B was plotted against time. Assuming first-order kinetics, the rate constant was then calculated from the slope of the line. The molar response factors were assumed to be unity.

The following general procedure was used for the degradation of methyl 6-aldehydo-glycopyranosides (I–VII). To the methyl 6-aldehydoglycopyranoside (10–20 mg) was added a known amount (5–10 mg) of internal standard, L-rhamnitol. Buffer solution (10 ml) of a desired pH was added. The solution was transferred to a glass stoppered test-tube which was heated in a constant water bath at 90 °C. At certain time intervals samples were withdrawn, cooled, neutralized, reduced with sodium borohydride and finally acetylated with acetic anhydride-pyridine 1:1 for 10 min at 90 °C. The obtained mixture was then submitted to GLC.

*Methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-*D*-glucopyranoside (VIII).* A solution of methyl 2,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-β-D-glucopyranoside [18] (20.0 g) in *N*,*N*-dimethylformamide (250 ml) was stirred with sodium azide (20.0 g) for 10.5 h at 100 °C. The reaction mixture was cooled, filtered and evaporated at 50 °C to a syrup which was dissolved in benzene (150 ml) and filtered to remove salts. Evaporation several times from toluene, treatment with charcoal in methanol, and crystallization of the ethanolic solution yielded 5.6 g (27 %) colourless crystals with m.p. 81–83 °C, $[\alpha]_D^{25}$ −35 °(*c* 0.5, chloroform). TLC analysis (solvent a) showed one pure substance, R_F 0.66 (yellow spot with sulfuric acid spray). (Found: C 45.16; H 5.52; N 12.14; O 36.93. Calc. for $C_{13}H_{19}N_3O_8$: C 45.21; H 5.55; N 12.17; O 37.07).

*Methyl β-*D*-gluco-hexodialdopyranoside-(1,5)*[19] *(III):* via *photolysis of methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-*D*-glucopyranoside (VIII).* Methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranoside (VIII) (0.5 g) was dissolved in benzene (150 ml) and photolysed under a slow stream of nitrogen until TLC examination of the reaction mixture (solvent a) revealed complete conversion (4 h). The pale yellow solution was evaporated to dryness. The residue was deacetylated by dissolving the residue in methanol (15 ml) and treating the solution with a catalytic amount of sodium methoxide solution (0.5 g sodium/100 ml ethanol) (2 ml) at room temperature. The yellow solution was evaporated to a syrup. Water (15 ml) and Dowex 50 W × 8 (H^+) 50–100 mesh (5 ml) was added and the solution was stirred for 2 h at room temperature. Removal of the resin by filtration gave a pale yellow solution which was treated with activated charcoal at 30 °C for 30 min. Filtration through celite 545 and evaporation of the water solution and drying under high vacuum yielded a clear glass (0.21 g) showing chromatographic data in accordance with those for methyl β-D-*gluco*-hexodialdopyranoside-(1,5).[19] Paper electrophoresis in buffer (b) gave M_{vanillin} 1.10. Reduction, hydrolysis, reduction, acetylation, and GLC analysis revealed a pure substance indistinguishable from an authentic sample of D-glucitol hexaacetate.

*Methyl 2,3-di-*O*-acetyl-6-chloro-6-deoxy-4-*O-

methyl-β-D-glucopyranoside (IX). Methyl 4-*O*-methyl-β-D-glucopyranoside[20] (4.0 g) was dissolved in *N,N*-dimethylformamide (40 ml) at 60 °C and methanesulfonyl chloride (15 ml) was added dropwise to the stirred solution, analogously to a method described by Evans *et al.*[18] After 10 h at 60 °C, the mixture was cooled in ice and methanol (40 ml) was added. pH was adjusted to 10 with solid sodium methoxide and the solution was filtered. The precipitated salts were washed several times with small portions of methanol. The solvents were evaporated at 50 °C. After evaporation several times with toluene, the residue was acetylated with acetic anhydride (12 ml) in pyridine (24 ml) over night. The mixture was treated with ice-water and evaporated. Treatment of the syrup with activated charcoal in hot chloroform, evaporation and recrystallization from ethanol gave colourless crystals (3.2 g; 54 %), m.p. 96–98 °C. TLC (solvent a), R_F 0.70; $[\alpha]_D^{25}$ −35° (*c* 0.5, chloroform). (Found: C 46.53; H 6.18; Cl 11.26, O 35.90. Calc. for $C_{12}H_{19}ClO_7$: C 46.38; H 6.16; Cl 11.40; O 36.04).

Methyl 2,3-di-O-acetyl-6-azido-6-deoxy-4-O-methyl-β-D-glucopyranoside (X). Methyl 2,3-di-*O*-acetyl-6-chloro-6-deoxy-4-*O*-methyl-β-D-glucopyranoside (IX) (3.2 g) was dissolved in *N,N*-dimethylformamide (35 ml) at 80 °C. Sodium azide (3.2 g) was added. The mixture was stirred for 16 h at 80 °C and worked up as described for VIII. Recrystallization from ethanol yielded colourless crystals (2.5 g), m.p. 112–114 °C. TLC (solvent a), R_F 0.70 (yellow spot with sulfuric acid spray). $[\alpha]_D^{25}$ −44° (*c* 0.5, chloroform). (Found: C 45.40; H 5.73; N 13.30, O 35.48. Calc. for $C_{12}H_{19}N_3O_7$: C 45.42; H 6.03; N 13.24; O 35.30).

Methyl 4-O-methyl-β-D-gluco-hexadialdopyranoside-(1,5)[21] *(IV)*: via *photolysis of methyl 2,3-di-O-acetyl-6-azido-6-deoxy-4-O-methyl-β-D-glucopyranoside (X).* Methyl 2,3-di-*O*-acetyl-6-azido-6-deoxy-4-*O*-methyl-β-D-glucopyranoside (X) (0.4 g) was dissolved in benzene (150 ml). The photolysis and work up procedures were performed as described for III. The resulting clear glass (0.24 g) had chromatographical data identical with those obtained previously for methyl 4-*O*-methyl-β-D-*gluco*-hexodialdopyranoside-(1,5). Reduction, hydrolysis, reduction acetylation, and GLC analysis revealed a pure substance indistinguishable from an authentic sample of 4-*O*-methyl-D-glucitol pentaacetate.

Degradation of the α- and β-isomers of methyl α-D-gluco-hexodialdopyranoside-(1,5) (II and III) in phosphate buffer (pH 6). Methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (II) (2.0 g) was dissolved in phosphate buffer of pH 6 (100 ml). The solution was heated on a water bath at 90 °C for 24 h. The position of the peak maximum in UV (253 nm) was similar to data obtained by Perlin *et al.*[8] After 24 h, when no starting material was left, the treatment was finished. The pH after the reaction was 6. The solution was extracted with ethyl acetate (3 × 200 ml). The water phase was evaporated to 30–40 ml and extracted with ethyl acetate (3 × 100 ml). The combined extracts were washed with water (100 ml), dried with sodium sulfate and evaporated to dryness. Column chromatography of the residue on silicic acid with dichloromethane-acetonitrile (1:1) as eluent gave a fraction containing 342 mg (19 %). TLC (solvent c) gave R_F 0.55. Paper electrophoresis in buffer b gave M_V 1.16 compared to M_V 1.04 for methyl α-D-*gluco*-hexodialdopyranoside-(1,5) (II): Part of the pure fraction (XI) was acetylated with acetic anhydride-pyridine at 25 °C overnight. After evaporation several times with benzene and purification with activated charcoal, a colourless syrup (XIII), which gave only one spot on TLC (solvent a), was obtained. The optical rotation was $[\alpha]_D^{25}$ +213° (*c* 3.0 methanol). The spectral characteristics for UV, IR, and NMR, of the syrup (XIII) were identical to those of an authentic sample. These data confirmed the structure of XIII as methyl 2,3-di-*O*-acetyl-4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5),[8] and obviously XI was methyl 4-deoxy-β-L-*threo*-hex-4-enodialdopyranoside-(1,5).

When part of XI was reduced with sodium borohydride in acetate buffer (pH 3–4) at 0 °C for 20 h, treated with Dowex 50 (H^+) ion-exchange resin and evaporated with methanol, a syrup (XV) was obtained. TLC: (solvent d), R_F 0.35 and optical rotation $[\alpha]_D^{25}$ +184° (*c* 0.5, methanol). Williams[25] reports $[\alpha]_D^{25}$ +192° (methanol) for methyl 4-deoxy-β-L-*threo*-hex-4-enopyranoside (XV), the expected reduction product.

In the same way methyl 4-deoxy-α-L-*threo*-hex-4-enopyranoside-(1,5) (XII) was obtained when methyl β-D-*gluco*-hexodialdopyranoside-(1,5) (III) was treated in buffer solution as above. Paper electrophoresis in buffer b gave M_V 1.23 for XII compared to M_V 1.10 for methyl β-D-*gluco*-hexodialdopyranoside-(1,5) (III). The acetate of XII, methyl 2,3-di-*O*-acetyl-4-deoxy-α-L-*threo*-hex-4-enodialdopyranoside-(1,5) (XIV), was identical to an authentic sample according to UV, IR, and NMR spectral data.[8]

Isomerisation of the α- and β-isomers of methyl D-gulo-*hexodialdopyranoside-(1,5) (V and VI) in phosphate buffer (pH 6).* A sample of V was treated with phosphate buffer (pH 6) and heated at 90 °C for 45 min (corresponding to 50 % conversion). After cooling, sodium borohydride was added and the solution was left at room temperature for 3 h. Treatment with Dowex 50 (H^+) ion exchange resin and evaporation from methanol yielded a syrup. Excess 0.25 M sulfuric acid was added and the solution was left on a water bath (90 °C) overnight. The cooled solution was treated with barium carbonate, filtered, and evaporated to a small volume. A sample of the syrup was examined by paper electrophoresis (buffer a) and by paper chromatography revealing the presence

of equal amounts of gulose and mannose (M_G 0.82 and M_G 0.72, respectively.) Another sample was acetylated with acetic anhydride-pyridine (1:1) for 10 min at 90 °C. The reduced and acetylated product was analyzed by GLC on a 3 % ECNSS-M column at 190 °C. Two peaks were observed which corresponded to glucitol hexaacetate and mannitol hexaacetate. Analogous chromatographic and electrophoretic data were obtained when VI was treated as above.

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REFERENCES

1. Theander, O. *Tappi 48* (1965) 105.
2. Theander, O. *Acta Chem. Scand. 12* (1958) 1879.
3. Theander, O. *Acta Chem. Scand. 12* (1958) 1887.
4. Theander, O. *Acta Chem. Scand. 18* (1964) 1297.
5. Pettersson, B. and Theander, O. *Unpublished results.*
6. Pettersson, B. and Theander, O. *Acta Chem. Scand. B 28* (1974) 29.
7. Horton, D., Luetzow, A. E. and Wease, J. *Carbohyd. Res. 8* (1968) 366.
8. Perlin, A. S., Mackie, D. M. and Dietrich, C. P. *Carbohyd. Res. 18* (1971) 185.
9. Luetzow, A. E. and Theander, O. *Sv. Papperstidn. 77* (1974) 312.
10. Theander, O. *Sv. Papperstidn. 61* (1958) 581.
11. Blears, M. J., Machell, G. and Richards, G. N. *Chem. Ind. (London)* (1957) 1150.
12. Theander, O. *Unpublished results.*
13. Beving, H. F. G. Luetzow, A. E. and Theander, O. *Carbohyd. Res. 41* (1975) 105.
14. Beving, H. F. G. and Theander, O. *Acta Chem. Scand. B 29* (1975) 577.
15. Pettersson, B. and Theander, O. *Acta Chem. Scand. 27* (1973) 1900.
16. Theander, O. *Acta Chem. Scand. 11* (1957) 1557.
17. Gomori, G. *Methods Enzymol. 1* (1955) 138.
18. Evans, M. E., Long, L. Jr. and Parrish, F. W. *J. Org. Chem. 33* (1968) 1075.
19. Assarsson, A. and Theander, O. *Acta Chem. Scand. 12* (1958) 1507.
20. Bouveng, H. O., Lindberg, B. and Theander, O. *Acta Chem. Scand. 11* (1957) 1788.
21. Assarsson, A. and Theander, O. *Acta Chem. Scand. 18* (1964) 727.
22. Llewellyn, J. W. and Williams, J. M. *Carbohyd. Res. 22* (1972) 221.

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