

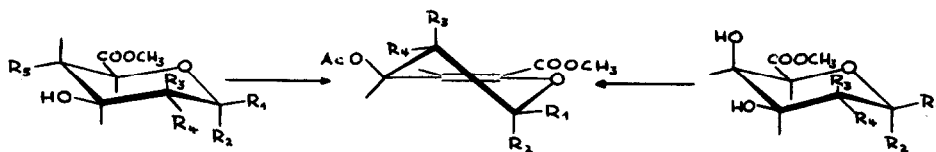
## β-ELIMINATION OF METHYL (METHYL HEXOPYRANOSID) URONATES

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Current interest in the degradation of polysaccharides containing (1 → 4) linked uronic acid residues by a base catalyzed β-elimination reaction (1,2) prompts us to report our findings on the different reaction rates of different uronic acids and some of their anomers. The anomers of methyl (methyl D-glucopyranosid) uronate (I,II), the anomers of methyl (methyl D-galactopyranosid) uronate (III,IV), and methyl (methyl α-D-mannopyranosid) uronate (V) and its 4-O-methyl derivative (IX) were subjected to β-elimination by refluxing 200 mg each of the uronates in acetic anhydride (6 ml) containing sodium acetate (100 mg). Excepting the 4-O-methyl derivative IX elimination occurred with all of the other derivatives .



I R<sub>1</sub> = R<sub>3</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>; R<sub>4</sub> = R<sub>5</sub> = OH

II R<sub>2</sub> = R<sub>3</sub> = H; R<sub>1</sub> = OCH<sub>3</sub>; R<sub>4</sub> = R<sub>5</sub> = OH

V R<sub>1</sub> = R<sub>4</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>; R<sub>3</sub> = R<sub>5</sub> = OH

IX R<sub>1</sub> = R<sub>4</sub> = H; R<sub>2</sub> = R<sub>5</sub> = OCH<sub>3</sub>; R<sub>3</sub> = OH

VI R<sub>1</sub> = R<sub>3</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>; R<sub>4</sub> = OAc

VII R<sub>2</sub> = R<sub>3</sub> = H; R<sub>1</sub> = OCH<sub>3</sub>; R<sub>4</sub> = OAc

VIII R<sub>1</sub> = R<sub>4</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>; R<sub>3</sub> = OAc

III R<sub>1</sub> = R<sub>3</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>; R<sub>4</sub> = OH

IV R<sub>2</sub> = R<sub>3</sub> = H; R<sub>1</sub> = OCH<sub>3</sub>; R<sub>4</sub> = OH

The reaction rates were followed by withdrawing and analyzing (g.l.c. (3) ) samples at intervals. This showed that the uronides were acetylated rapidly, whereupon acetic acid was eliminated to yield the corresponding methyl (methyl 4-deoxy-hex-4-enopyranosid) uronates. Discoloration, indicating further degradation, occurred simultaneously with the elimination. The percentages of elimination were calculated from the triangulated peak areas (4). The relative rates of elimination were found to follow the order:

β-galacto > β-gluco > α-manno > α-galacto > α-gluco

giving 82.8 %, 52.3 %, 41.1 %, 35.9 %, and 9.6 % elimination, respectively, after a reaction time of 5 h.

The stereochemistry at the reaction centres C-4 and C-5 (trans- or cis-elimination) as well as steric factors influencing the conversion of chair to half-chair conformation, which accompanies the formation of

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of the double bond, seem to be responsible for these differences. The results suggest that the relative configurations at C-1 and C-2 of the methyl (methyl 2,3,4-tri-O-acetyl-hexopyranosid) uronates affect the rate of  $\beta$ -elimination to approximately the same extent as the stereochemistry at the reaction centres C-4 and C-5.

In reactions on a preparative scale the unsaturated uronides were separated by column chromatography (silica gel, Benzene / acetone 9:1 v/v) and purified by kugelrohr distillation (b.p. 120-130°C/0.03 mm Hg). The u.v. spectra showed strong absorption at max 233 nm.

Methyl (methyl 2,3-di-O-acetyl-4-deoxy- $\beta$ -L-threo-hex-4-enopyranosid) uronate (VI) (5):

(Prepared from III; reaction time 9h; yield 52,7 %). Colorless syrup;  $n_D^{24}$  1.4751;  $\alpha_D^{29} + 259.9^\circ$  (c 1.124 in methanol).

Methyl (methyl 2,3-di-O-acetyl-4-deoxy- $\alpha$ -L-threo-hex-4-enopyranosid) uronate (VII) (5):

(Prepared from IV; reaction time 8h; yield 92.5 %). Colorless prisms, m.p.(corr.) 90.5-91.0° (from benzene/heptane);  $\alpha_D^{26} + 34.0^\circ$  (c 1.160 in methanol).

Methyl (methyl 2,3-di-O-acetyl-4-deoxy- $\beta$ -L-erythro-hex-4-enopyranosid) uronate (VIII) (5):

(Prepared from V; reaction time 15h; yield 45.4 %). Colorless syrup;  $n_D^{24}$  1.4698;  $\alpha_D^{26} + 203.7^\circ$  (c 0.902 in methanol).

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References

1. C.W. McCleary, D.A. Rees, J.W.B. Samuel and J.W. Steele, Carbohydr. Res., 5, 492 (1967).
2. J. Kiss, 5th Int. Symposium on the Chemistry of Natural Products, London, July 1968.
3. VARIAN-AEROGRAPH 1200, injection temperature: 200°C, oven temperature: 170°, FID, carrier gas: 24 ml N<sub>2</sub>/min, column: 5 ft 1/8 in stainless steel, 5 % SE-30 on 60-80 mesh Chromosorb W (AW/DMCS).
4. The FID response was calibrated with mixtures of the saturated and the unsaturated acetates at different ratios.
5. This compound was gas-chromatographically pure and gave satisfactory analyses.