Hydrolysis of Periodate Oxidized-reduced Glycosides
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The Smith degradation of polysaccharides, which is a sequence of reactions comprising oxidation, borohydride reduction and hydrolysis of the resulting polyalcohol under mild conditions, has become an important tool in polysaccharide chemistry. The conditions of the hydrolyses are critical, and Smith and VanCleve studied the rate of hydrolysis of the mixed acetal I, prepared from methyl-α-D-glucopyranoside. No other model substances seem to have been studied. Dutton and Gibney have, however, recently shown how the hydrolysis of the polyalcohol could be monitored by GLC of the products.

We now report hydrolysis studies on I, II, and III, the latter prepared from methyl 2- and 4-O-methyl-α-D-glucopyranoside, respectively. These glycosides, which are known substances, were prepared by conventional methods. After oxidation with periodate in aqueous methanol, they were reduced with borohydride and the products purified by distillation or preparative TLC. The products which were amorphous, were chromatographically pure (TLC).

The acetate derivatives were also pure (GLC) and their NMR and mass spectra were in agreement with the postulated structures. The origin of some primary fragments on MS are indicated in the formulae below.

The hydrolyses of I, II, and III, each at three different temperatures, were followed polarimetrically. Inactive products should be formed from I, but II and III should give optically active products, in accordance with the experimental finding. Because of the rather low change in optical rotation during the hydrolysis, the rate constants and activation energies (Table I) may be subject to rather large errors. Whilst I and III are hydrolysed at about the same rate, II reacts about ten times slower. This is attributed to the presence in II of electron attracting groups in both the α- and β-positions to the acetal carbon atom. The corresponding values for methyl α-D-glucopyranoside at 40°, extrapolated from published values, are also given in Table I. The differences in rate of hydrolysis for the acyclic acetals and the glucoside are considerable and it should be possible to hydrolyse the former completely without affecting the latter. The activation energy is higher for the glucoside, and the difference in rate is consequently enhanced at low temperatures. Smith and his co-workers also used comparatively strong

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Table I. Rate constants and activation energies for the acid hydrolysis of the mixed acetals I, II, and III.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
<th>k × 10^4 sec⁻¹</th>
<th>E kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>11.30</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>40</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.89</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>20</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>12.90</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>40</td>
<td>0.00005</td>
<td>35.1</td>
</tr>
</tbody>
</table>

\[
\alpha-D\text{-glucopyranoside (7.6 g) and silver oxide (6.4 g) in dimethylformamide (60 ml), kept below 4}^\circ\text{C by external cooling. The mixture was allowed to reach room temperature and stirring was continued overnight. The mixture was filtered, concentrated and fractionated on a silicie acid column (9 × 50 cm), using toluene-ethanol (1:1) as irradiant. The eluate was monitored polarimetrically and by TLC. The third component eluted (1.8 g) was pure methyl 4,6-O-benzylidene 2-O-methyl-\alpha-D-glucopyranoside, which after crystallization showed m.p. 169–170° and \([\alpha]_D^{24} + 97^\circ\text{ (c 0.8, chloroform), in good agreement with published values,}^4\text{ This substance was hydrogenated (H_2/Pd) and the product crystallized from ethyl acetate, giving the title compound (0.7 g), m.p. 147–148°, }[\alpha]_D^{24} + 158^\circ\text{ (c 1.0, water), in good agreement with published values}.^6

Methyl 4-O-methyl-\alpha-D-glucopyranoside was prepared essentially as described by Whistler and coworkers\textsuperscript{1} and showed m.p. 95–96°, \([\alpha]_D^{24} + 172^\circ\text{ (c 0.8, water)}\text{.}

Preparation of the mixed acetals I, II, and III. Sodium metaperiodate (22 g) in water (150 ml) was added to a solution of methyl \alpha-D-glucopyranoside (10 g) in methanol (700 ml). The mixture was kept in the dark at room temperature for 15 h, filtered and concentrated. The resulting syrup and sodium borohydride (15 g) in water (200 ml) was kept for 12 h at room temperature, excess borohydride was decomposed with acetic acid and the solution concentrated. Boric acid was removed by codistillations with methanol and the product extracted with ethanol, concentrated and distilled at 200–210°/0.2 mm. The resulting syrup (3.0 g), \([\alpha]_D^{24} + 13^\circ\text{ (c 2.45, water)}, consisted of chromatographically pure I (TLC, chloroform-ethanol, 7:3). The acetate, which gave a single peak on TLC, showed the following peaks on NMR: 5.19 (t, 1H) proton at C-1 of the original glucoside, 5.70–5.95 (m, 7H) protons at C-2, C-4, C-5 and C-6, 6.55 (s, 3H) OCH_3, 7.92 (s, 9H) OOCCH_3. It gave the following ions on MS (relative intensities in brackets): 43(100), 45(4), 99(2), 103(2), 117(10), 145(1), 159(12).

The mixed acetals II and III were prepared analogously, except that half of the molar amount of periodate was used and the products were not distilled, but purified by TLC (chloroform-ethanol 7:3). They were both obtained as chromatographically pure syrups and their acetates gave single peaks on TLC.

II, [\alpha]_D^{24} + 13^\circ\text{ (c 2.8, water). NMR of the acetate: 5.40 (d, 1H) proton at C-1, 5.65–5.90 (m, 8H) protons at C-2, C-3, C-4, C-5 and C-6, 6.52 (s, 3H) and 6.53 (s, 3H) two OCH_3, 7.92 (s, 9H) OOCCH_3. MS of acetate: 43(100), 99(9),

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Studies on Orchidaceae
Alkaloids

XXXVI.* Alkaloids from Some Vanda and Vandopsis Species

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Esters of 1-hydroxymethylpyrrolizidine have previously been isolated from orchid extracts. Laburnine acetylate (I) has been isolated from Vanda cristata Lindl.1 and more complex esters from Phalaenopsis8
and Liparidinae 3-4 species. We now report similar studies on some other Vanda and closely related Vandopsis species.

From Vandopsis lissoclades Pfitz. the alcohols laburnine (III) and lindelofidine (IV) were isolated, together with the corresponding acetates I and II, in the exo/endo ratios 1/3. From Vandopsis gigantea Pfitz. the same alcohols and acetates were isolated in the exo/endo ratios 10/1. Laburnine acetylate (I) has been isolated

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1: R + CH₂OAc, R' + H
II: R + H, R' + CH₂OAc
III: R = CH₂OH, R' + H
IV: R + H, R' + CH₂OH

from Vanda hindsii Lindl., and I and III from Vanda helvola Bl. An extract of Vanda luzonica Loher contained either I or its enantiomer (GLC-MS). A small amount of hygrine was detected (GLC-MS) in an extract of Vandopsis parishii Schlr.

In some of the above investigations a modified reineckate procedure was used to purify and quantify small amounts of

* For number XXXV in this series, see Ref. 6.

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