Preliminary communication

Formation of methyl 2-carboxy-β-D-pentofuranosides by oxidation of methyl β-D-glucopyranoside with oxygen in alkaline, aqueous solution

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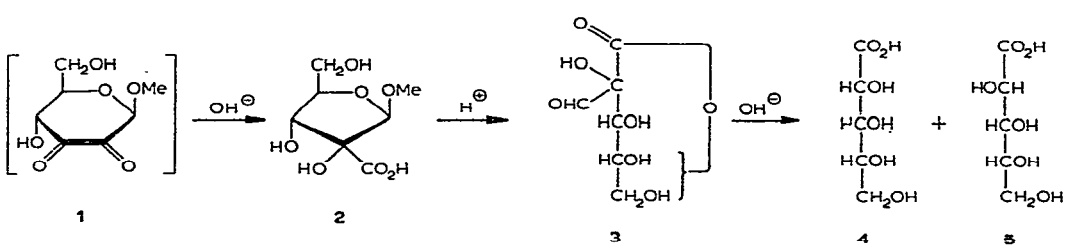
In connection with model studies of the bleaching of pulp by oxygen, a solution of methyl β-D-glucopyranoside in 0.5M sodium hydroxide was treated with oxygen (6 atm) at 95° for 200 h in a Teflon-lined autoclave. The products were fractionated by anion-exchange chromatography (Dowex-1 X10, 100–200 mesh) with 0.5M sodium hydroxide as eluant. The main fractions were adjusted to pH 7 by addition of cation-exchange resin, and small samples were examined by paper chromatography and paper electrophoresis, first directly and then after complete removal of sodium ions.

One of the sodium salt fractions (yield, *ca.* 8% by weight of the reacted starting material; $[\alpha]_D$ −44°) gave two spots (M_G 0.91 and 0.78) in borate (pH 10) electrophoresis, which reacted positively with silver nitrate. The following results suggested that the fraction consisted of the sodium salts of two methyl 2-carboxy-β-D-pentofuranosides (2), obtained by rearrangements of an oxidation product **1**. Part of the sodium salt fraction was transformed into the trimethylsilyl ethers and esters by treatment with bis(trimethylsilyl)trifluoroacetamide[1]. G.l.c. of the product revealed two major peaks, and the mass spectra of the corresponding compounds were almost identical: *m/e* 73 (100%, base peak), 89 (6), 103 (14), 133 (35), 147 (40), 217 (7), 247 (10), 305 (8), 333 (65), 346 (7), 421 (2), 436 (8), 449 (1.5), 465 (0.5), 481 (1.5), 496 (0.2, M^+).



1 2 3 4 5

The ions of mass M–31 and M–47 (= M–15–32) suggested the presence of a methoxyl group. The optical rotation was highly negative, indicating a β-furanosidic rather than a β-pyranosidic structure. The n.m.r. spectrum of the salt mixture (in D_2O) showed two distinct peaks at τ 5.55 and 5.65 assigned to the glycosidic methoxyl groups, and two singlets at τ 5.17 and 5.27 for the anomeric protons, indicating the absence of a proton at C-2.

After treatment of the salt fraction with dilute acetic acid or excess of cation-exchange resin, the two acidic glycosides disappeared and methanol (identified by g.l.c.) and a lactone mixture were formed. The lactones were deduced to be of structure **3** by the mode of their formation and from the following evidence. On paper electrophoresis in acetate buffer (pH 4.5), one lactone spot and one minor acid spot were obtained, both of which reacted strongly with the dinitrophenylhydrazine reagent indicating the presence of an aldehydo or keto group. The mass spectrum of the trimethylsilyl derivatives of the lactones showed a peak for the expected molecular ion (*m/e* 392).

When an aqueous solution of the lactones was treated with an excess of sodium hydrogen carbonate at 20° for 2 h, the main products obtained were arabinonic (**5**) and ribonic (**4**) acids, as demonstrated by paper chromatography and g.l.c.–mass spectrometry of their trimethylsilyl derivatives. The fact that a carbonyl group is readily removed suggests that the lactones contain a formyl group in the α-position to the lactone carbonyl group (*cf.* formula **3**). The formation of **4** and **5** indicates the configurations at C-3 and C-4 of the lactones.

Small amounts of another acid were, however, obtained by the addition of sodium borohydride to the hydrogen carbonate-treated compound **3**. The trimethylsilyl derivative of the lactonised reduction product showed a molecular ion at *m/e* 466 in its mass spectrum (the spectrum obtained was superimposed on that of arabinonic acid). The fragmentation pattern of the trimethylsilyl derivative of the acyclic form indicated a 2-*C*-(hydroxymethyl)-pentonic acid, namely the expected reduction product of the compound **3**. The abundant ion of mass 394 for the acyclic derivative, as well as a very abundant ion of mass 436 (M–30) in the lactone spectrum, correspond to predictable McLafferty-type rearrangements of a trimethylsilyl group[1] and give strong evidence for the assigned structures. Mass spectrum of the derivative of the acyclic form: *m/e* 73 (100%, base peak), 103 (40), 147 (35), 205 (13), 217 (39), 218 (10), 277 (5), 307 (25), 333 (8), 359 (3), 394 (2), 395 (9), 407 (2), 421 (1), 433 (3), 434 (2), 435 (2), 467 (0.2), 469 (0.2), 479 (0.2), 481 (0.3), 493 (0.2), 494 (0.2), 495 (0.3), 496 (0.2), 523 (0.2), 524 (0.2), 525 (0.3), 526 (0.2), 538 (0.2), 613 (0.8, M^+–15), 614 (0.6), 615 (0.3).

These results indicate that the acids formed by oxygen oxidation have the structure **2**. There are also indications of the presence of smaller amounts of other carboxy-pentofuranosides. It is notable that the two keto groups in compound **1** must have been introduced simultaneously, since the 2-keto and 3-keto derivatives of methyl β-D-gluco-pyranosides are known[2] to be extremely sensitive towards β-elimination at C-1.

REFERENCES

1 G. Petersson, *Org. Mass Spectrom.*, 4 (1972) 663.
2 O. Theander, *Acta Chem. Scand.*, 12 (1958) 1897.