BRIEF COMMUNICATIONS

POLYSACCHARIDES OF Eremurus.

XVI. DETERMINATION OF THE POSITION OF THE OAC

GROUPS IN THE GLUCOMANNANS OF Eremurus turkestanicus

AND E. lactiflorus

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We have previously put forward structures for the glucomannans isolated from the tuberous roots of *Eremurus turkestanicus* and *E. lactiflorus* [1, 2]. According to their IR spectra, the glucomannans of these plants are partially acetylated.

In the 13 C NMR spectrum of the glucomannan from E. lactiflorus, there are weak signals at 21.5 and 22 ppm and 174—175 ppm, relating to the resonance of the methyl and carboxy groupings of acetates [3].

In the present communication we give information on the determination of the positions of the OAc groups in the glucomannans.

The glucomannan from E. turkestanicus (2 g) was treated with an excess of phenyl isocyanate by Bouveng's method [4] and the resulting phenylcarbamate [N 8.35%; $[\alpha]_D^{20}$ -88° (c 1.0; DMF). IR spectrum (cm⁻¹): 1735 and 1250 (O-Ac); 1715 (ester-amide); 1602 (phenyl)] was de-acetylated and it was then methylated by Kuhn's method [5], the acetyl groups being replaced by methyls. The phenylcarbamate groups of the product obtained were eliminated by reduction with lithium tetrahydroaluminate. The partially methylated glucomannan so obtained was hydrolyzed (2 N $_2$ SO₄, 100°C, 14 h), and glucose and a partially methylated sugar with $_1$ 0.8 were detected in the hydrolysate by PC in the butan-1-ol-pyridine-water (6:4:3) system. Part of the sugar was demethylated by a standard method [6], and mannose was detected by PC and GLC. Another part of the sugar was subjected to methanolysis and acetylation.

The mass spectrum of the resulting acetylated methyl glycoside had the following peaks, m/z: 303 (M - OCH $_3$) (A), 261(M - Ch $_2$ OAc), 242, 232 (M - 60 - 42), 201 (A - 60 - 42), 169 (A - 60 - 42 - 32), 159, 157, 116, 112, and 77, which is in agreement with literature information [7] for the 3-0-methyl derivative of mannose. The formation of this substance shows that the OAc groups are localized on the C $_3$ atoms of some of the mannose units of the glucomannan.

The presence of the OAc groups at C_3 of some of mannose residues in the glucomannan from E. lactiflorus was established similarly and by the same methods.

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