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Structure of Aconitan A, a Hypoglycemic Glycan of *Aconitum carmichaeli* Roots*

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We have recently isolated four glycans possessing hypoglycemic activity, aconitans A, B, C, and D, from the crude drug "bushi" (aconite), the roots of *Aconitum carmichaeli* DEBEAUX (Ranunculaceae). Structural examination of the main polysaccharide, aconitan A, is described in this paper.

Gel chromatography of aconitan A gave a value of 8700 for the molecular weight. Glucose was identified as the only component and nitrogen was absent. This polysaccharide was strongly dextrorotatory ($[\alpha]_D$+190°) and its ^{1}H-NMR spectrum exhibited an anomeric doublet (J=3 Hz) at δ 4.98, demomstrating the D-glucose residues to be α-linked.

Seven major signals visible in the ^{13}C-NMR spectrum, at δ 63.2, 68.3, 72.2, 72.9, 74.1, 76.1, and 100.4, were assignable to C-6 (free), C-6 (linked), C-4, C-5, C-2, C-3, and C-1, respectively, indicating that α-D-glucose residues are linked at the 1 and 6 positions. The appreciable intensity of the signal for C-6 carbon having a free hydroxyl group was indicative of branching in aconitan A. However, the branching position could not be deduced from the ^{13}C-NMR spectrum at this stage, because branching was infrequent.

Aconitan A was methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated product was successively hydrolyzed, reduced, and acetylated. The partially methylated glucitol acetates thus obtained were analyzed by gas-liquid chromatography-mass spectrometry. Three products were identified: 2,3,4,6-tetra-*O*-methyl-, 2,3,4-tri-*O*-methyl-, and 2,4-di-*O*-methyl-D-glucitol acetates, in the molar ratio of 1.2 : 9.0 : 1.0, showing that aconitan A is branched through O-3.

When aconitan A was oxidized with periodate, 1.6 mol of periodate per mol of suger residues was consumed, with liberation of 0.8 mol of formic acid. The periodate-oxidized product was successively reduced, hydrolyzed, and analyzed, the yield of residual glucose being 5.8%.

As it is known that the (1→6)-glucosidic linkage is less stable to acetolysis than the (1→3)-linkage, aconitan A was acetolyzed with acetic anhydride-acetic acid-sulfuric acid. The acetolysis product was deacetylated and analyzed by thin-layer chromatography and the trimethylsilylated products were examined by GLC. Both glucose and nigerose were

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detected, and determined to be in the molar ratio of 19 : 1. No component other than glucose and nigerose was found in the acetolysis product.

From these results, it may be concluded that aconitan A is mainly composed of α-(1→6)-linked D-glucopyranose residues and has branches linked, in part, through O-3. In respect to the degree of branching, the methylation analysis and the Smith degradation show some apparent differences. The acetolysis results better support the value obtained by Smith degradation than does the methylation analysis. Aconitan A is concluded to be composed of ~54 glucose residues having three branching points.