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Preliminary communication

Synthesis of a derivative of D-kijanose (2,3,4,6-tetradeoxy-4-methoxycarbonylamino-3-*C*-methyl-3-nitro-D-*xylo*-hexopyranose)

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D-Kijanose[1] (or D-tetronitrose[2]) (**1**), a component of kijanimicin[3] and tetrocarcins A and B[2,4], is one of a novel group of methyl-branched nitro sugars found in antibiotic substances. We have declared[5] an interest in the synthesis of D-kijanose (**1**) by a route in which reduction of the keto sugar **2** constituted a key step. The yield of methyl 2,3,6-trideoxy-3-*C*-methyl-3-trifluoroacetamido-α-D-*xylo*-hexopyranoside (**7**) subsequently obtained in this step turned out to be unacceptably low, so that an alternative route was devised from the 3-acetamido analogue **3**, previously used in our synthesis[5,6] of D-rubranitrose (**4**) (from rubradirin[7]).

N-Deacetylation of **3** with calcium in liquid ammonia[8] gave **5**, which was immediately converted into **7**, m.p. 79–80°, $[\alpha]_D$ +54° (*c* 1, chloroform), in 74% overall yield *via* the corresponding 4-trifluoroacetate **6**. The methanolysis of **6** was markedly accelerated in the presence of silica gel. Methanesulphonylation of **7** then gave methyl 2,3,6-trideoxy-4-*O*-methanesulphonyl-3-*C*-methyl-3-trifluoroacetamido-α-D-*xylo*-hexopyranoside (**8**), m.p. 89–90°, $[\alpha]_D$ +86° (*c* 1.1, chloroform), in 96% yield. Treatment of **8** with sodium borohydride in anhydrous ethanol at room temperature for 3 h afforded, after chromatography on silica gel with acetone, a high yield of methyl 2,3,4,6-tetradeoxy-3,4-epimino-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**9**), $[\alpha]_D$ ~+76° (*c* 0.8, diethyl ether), as a volatile oil contaminated with traces of solvent**. In this step, reductive cleavage of the *N*-trifluoroacetyl group from **8** is followed by intramolecular displacement of the methanesulphonyloxy group by the amino group so exposed.

Opening of the aziridine ring of **9** with sodium azide in refluxing aqueous ethanol containing ammonium chloride[9] furnished, after chromatography on silica gel with ethyl acetate, methyl 3-amino-4-azido-2,3,4,6-tetradeoxy-3-*C*-methyl-α-D-*xylo*-hexopyranoside (**11**, 35.5%), m.p. 38–39°, $[\alpha]_D$ +204° (*c* 0.6, chloroform), and its regioisomer **10** (8.3%). The p.m.r. spectrum of **11** {lit.[10] m.p. 37.5–38.5°, $[\alpha]_D$ +186.5° (chloroform)} was indistinguishable from that reported[10] in connection with a synthesis of methyl α-D-kijanoside (**12**), which confirmed that natural kijanose (**1**) belongs to the D series. Whereas the combined yield of **10** and **11** is comparable to that obtained from **9** by the Japanese workers, the proportion of the desired regioisomer **11** is decidedly more

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Attempts to remove the last traces of solvent from **9 under reduced pressure resulted in severe loss of material.

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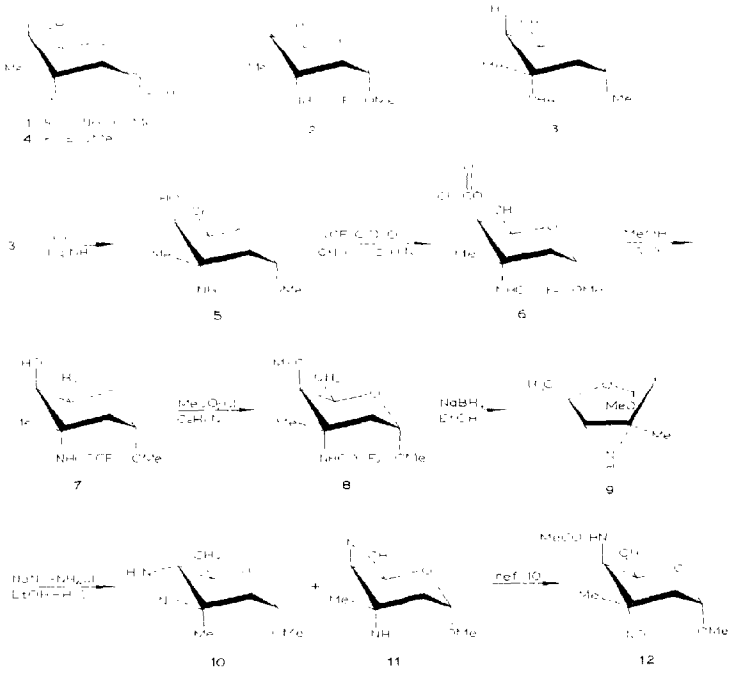

favourable than that (**10**:**11**, 2:3) reported[10]. Since **11**, in which the nitrogen functionalities can be manipulated independently, has already been transformed[10] into methyl α-D-kijanoside (**12**), the above sequence constitutes a formal synthesis of this rare-sugar derivative.

One notable advantage of our approach, which differs from that previously described[10] (from methyl α-D-mycaroside), is that derivatives of both D-kijanose and D-rubranitrose[6] (**4**) are accessible from the same precursor **3**[5].

New compounds had elemental analyses and/or spectroscopic properties in agreement with the structures assigned.

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