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Preliminary communication

Syntheses of L-rubranitrose (2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-L-*xylo*-hexopyranose) and the naturally occurring D enantiomer

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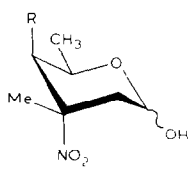
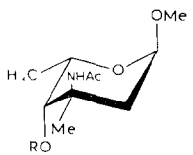
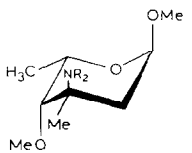
Rubranitrose[1] (from rubradirin[2]) is one of three novel, branched-chain nitro sugars that have been found as components of antibiotics in recent years. An X-ray crystallographic study[1] of the β-acetate revealed the relative stereochemistry of rubranitrose to be that of a 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-*xylo*-hexopyranose, and, on the basis of its c.d. spectrum, rubranitrose was assigned to the L series. Subsequently, rubranitrose was shown[3] to possess the same absolute configuration as D-kijanose (or D-tetronitrose[4]) (1)**, so that its correct structure is 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-D-*xylo*-hexopyranose (2).



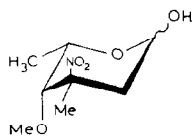
1 R = $NHCO_2Me$
2 R = OMe



3 R = H
4 R = Me



5 R = H
6 R = O



7

Before this new evidence came to light, we had embarked on a synthesis of L-rubranitrose (7) based on methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*xylo*-hexopyranoside[5] (3), a derivative of the novel, branched-chain amino sugar of antibiotic A35512B[6]. Methylation[7] of 3 gave methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-α-L-*xylo*-hexopyranoside (4, 83%), m.p. 84–85°, $[\alpha]_D$ −125° (*c* 0.5, chloroform), which we planned to take along the route 4 → 5 → 6 → L-rubranitrose (7). Whereas 4 resisted all attempts to hydrolyse the acetamido group using a variety of strong bases under aqueous conditions, *N*-deacetylation was readily accomplished with calcium in liquid am-

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**The absolute configuration of 1 has been confirmed by a recent synthesis of methyl α-D-kijanoside[4].

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monia[8] to give methyl 3-amino-2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-α-L-*xylo*-hexopyranoside (**5**), $[\alpha]_D$ ~−165° (*c* 0.7, chloroform), in 84% yield. Oxidation of **5** with *m*-chloroperoxybenzoic acid in boiling dichloromethane then furnished methyl 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-α-L-*xylo*-hexopyranoside (**6**, 69%), m.p. 92–93°, $[\alpha]_D$ −171° (*c* 0.7, chloroform), which, on hydrolysis with 0.05M sulphuric acid in aqueous 1,4-dioxane at ~90°, liberated L-rubranitrose (**7**), m.p. 152–154°, $[\alpha]_D$ −114.5° (7 min) → −83° (*equil.*; *c* 0.4, ethanol); lit.[1] (D enantiomer), m.p. 150–153°, $[\alpha]_D$ +127° → +86° (*equil.*; *c* 1, ethanol). An alternative route to **7** has been outlined recently by Yoshimura and coworkers[9].

Consequently, our recent synthesis[10] of methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-α-D-*xylo*-hexopyranoside (the mirror image of **4**) can be regarded as a formal synthesis of D-rubranitrose (**2**), although completion of this work, along the lines indicated above, is presently under way. Ironically, *N*-acetylation of the amino group at the branch-point was discarded in favour of *N*-trifluoroacetylation in another projected route[10] to D-rubranitrose (**2**), because the latter protecting-group is easier to remove. Now that it can be removed efficiently, the more robust *N*-acetyl group is preferred, since it is better suited to some of the earlier transformations involved.

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

NOTE ADDED IN PROOF

D-Rubranitrose (**2**), prepared as indicated above, had mp. 154–156°, $[\alpha]_D$ +115° (7 min) → +86° (*equil.*; *c* 0.5, ethanol).

ACKNOWLEDGMENTS

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