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# A Convenient Approach to the Synthesis of Glycosphingolipids *via* the Acidic Decyclization of Hexo-*O*-acetyl-D-gentiobial

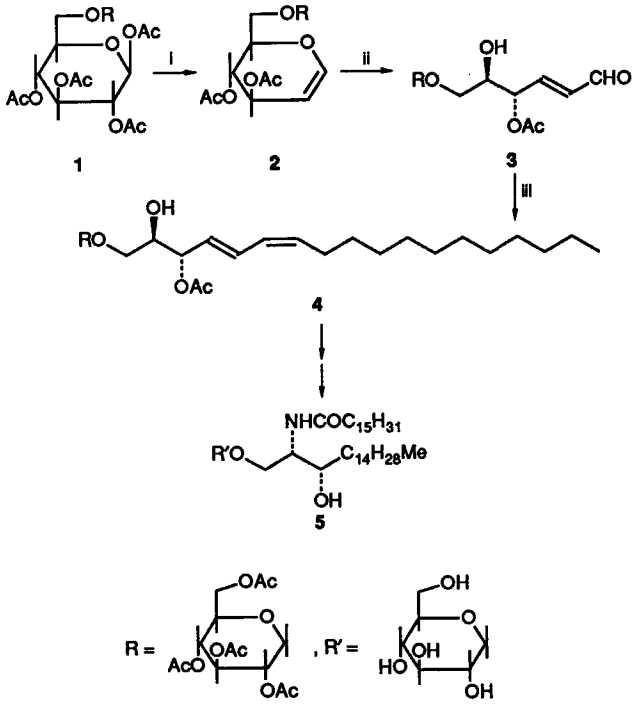
**Aleksander G. Tolstikov, Oleg F. Prokopenko, Radik Kh. Yamilov and Genrikh A. Tolstikov***

*Institute of Chemistry, Bashkirian Research Centre, Ural Department of the USSR Academy of Sciences, Ufa SU-450054, USSR*

The mercury sulphate catalysed acidic opening of the dihydropyran ring in hexa-*O*-acetyl-D-gentiobial **2**, resulting in (2*E*,4*S*,5*R*)-4-acetoxy-5-hydroxy-6-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)hex-2-enal **3** was employed as the key transformation in the synthesis of *O*-glycosides, which are precursors of glycosphingolipids.

In an earlier report[1] we showed that the acid-induced opening of the dihydropyran ring in hexa-*O*-acetyl-D-lactal did not break the 1→4 glycoside bond, and led to the *O*-glycosylated α,β-unsaturated diacetoxyaldehyde. The akenation of the latter paved the way to the synthesis of *O*-glycosides with polyhydroxopolyene aglycones. The specific aim of our research was to apply this method to synthesize the precursors of glycosphingolipids, *i.e.* for the first time we implemented similar transformations for a series of disaccharide derivatives containing 1→6 bonds.

According to the method described for hexa-*O*-acetyl-D-lactal,[2] the starting compound hexa-*O*-acetyl-D-gentiobial **2** was prepared in 65% yield from the readily available octa-*O*-acetyl-D-gentiobiose **1**. The glycal **2** was




**Scheme 1** *Reagents and conditions*: i, HBr, AcOH, 15 °C, 2 h; Zn, 50% AcOH, 3 h; ii, 5 mmol $dm^{-3}$ $H_2SO_4$, $HgSO_4$, dioxane, 25 °C, 2 h; iii, $BrPh_3PC_{12}H_{25}$, $Bu^nLi$, tetrahydrofuran, −78→0 °C, 1 h

treated with 5 mmol $dm^{-3}$ $H_2SO_4$ in the presence of a catalytic amount of $HgSO_4$ in dioxane to yield 40% of the aldehyde **3**.† The alkenation of **3** with dodecylidenetriphenylphosphorane gave a 28% yield of (2*R*,3*S*,4*E*,6*Z*)-3-acetoxy-2-hydroxy-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)octadeca-4,6-diene **4**, a close precursor of (2*S*,3*S*)-glycosphingolipid **5**.

In conclusion, the decyclization of tetra-*O*-acetyl-D-gentiobial, followed by the alkenation of the ring-opened product provides a convenient synthetic method for precursors of cerebrosides and of different glycosylated systems.

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## References

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2 T. L. Harris, R. W. Herbert, E. L. Hirst, C. E. Wood and H. L. Woodward, *J. Chem. Soc.*, 1936, 1403.

† *Spectral assignments* for **3**: $[\alpha]_D^{20}$ = 12.3° (*c*, 2.0, $CHCl_3$); $^{13}C$ NMR ($CDCl_3$) δ 20.50, 20.68 (5 $CH_3$, Ac), 61.84 (C-6′), 68.37 (C-2′), 70.75, 71.23, 71.35, 72.15, 72.28, 72.54 (C-4–C-6, C-3′–C-5′), 101.15 (C-1′), 132.92 (C-2), 150.67 (C-3), 169.37, 169.70, 170.18, 170.25, 176.59 (5 CO, Ac) and 192.89 (C-1).