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Isolation and characterisation of an unexpected byproduct in the regioselective butane diacetal protection of α-methyl galactopyranoside

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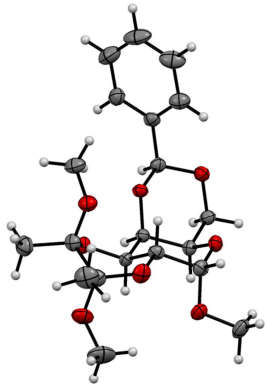
Abstract: The regioselective protection of both methyl galactopyranoside anomers at the 2 and 3-positions as the butane diacetal (BDA) is well known. Here we describe the formation of an unexpected byproduct, which mainly occurs when α-methyl galactopyranoside is reacted with 2,3-butanedione under BF_3•OEt_2 catalysis. The structure of the byproduct, which did not arise from anomerisation to the β-anomer or from BDA formation at the galactopyranoside 3,4-positions,, was elucidated by NMR and X-ray crystallographic analysis, and proved to be the expected BDA protected galactopyranoside, but in which the stereochemistry of both its BDA acetal centres are inverted. Interestingly, the conformation of the resulting six-membered BDA ring was distorted to a skew boat conformation in order to maintain anomeric stabilisation.

Keywords: galactose, butane diacetal, regioselective protection, conformation

Graphical abstract:



Highlights:

- selective butane diacetal protection of methyl galactopyranoside
- characterisation of a byproduct
- twist-boat butane diacetal conformation
- anomeric effect is the cause of significant six-membered ring deformation