

MEM GROUP AS A SELECTIVE PROTECTIVE GROUP FOR THE
HYDROXYL FUNCTIONS OF CARBOHYDRATES : APPLICATION
FOR THE SYNTHESIS OF A GLUCOTRISACCHARIDE

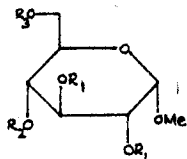
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The MEM group was shown to be a protecting group for hydroxyls in carbohydrates¹. The relative reactivity of hydroxyl groups in carbohydrates is complex². Steric and electronic factors influence the reactivity of hydroxyl towards a variety of reagents and it is often possible to exploit these factors to achieve protection of specific hydroxyl groups in polyols. Here we present the first report of the MEM group as a selective ether for the primary hydroxyls of hexopyranosides.

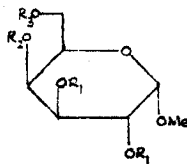
The D-glucopyranosides 2 and 4 underwent selective etherification with equimolar quantities of the tertiary amine and MEM chloride to give the corresponding 6-MEM 4-hydroxy derivatives 3 and 5 in yield of 85 and 88% respectively. The galactopyranosides 8 and 10 underwent similar etherification to give compounds 9 and 11 in good yield. Even methyl α -D-glucopyranoside 1 and methyl α -D-galactopyranoside 7 underwent selective etherification to yield the 6-MEM ethers 6 and 12 in 70% yield. Using this selectivity the branched glucotrisaccharide O- β -D-Glucopyranosyl - (1 \rightarrow 4)-O- [β -D-glucopyranosyl (1-6)] - Me α - D-glucopyranoside 18 was synthesised. Compound 4 was prepared by standard reactions (1 \rightarrow 13 \rightarrow 14 \rightarrow 4). This underwent selective etherification to give compound 5, which was reacted with tetra-O-acetyl- α -D-glucopyranosyl bromide and silver triflate in a mixture of benzene and nitromethane to give the disaccharide 15 (90% yield). The 6-MEM group was deblocked with ZnBr₂ to give the disaccharide 16 (85% yield). Compound 16 was condensed with another mole of glucosyl bromide to give the trisaccharide 17 (85%). All ester groups were removed by treatment with NaOMe to give the desired β , β linked glucotrisaccharide 18 in 95% yield. All compounds had ¹H and ¹³C n.m.r. spectra in accordance with assigned structures.

References

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- (1) $R_1 = R_2 = R_3 = H$
 (2) $R_1 = Me \quad R_2 = R_3 = H$
 (3) $R_1 = Me \quad R_2 = H \quad R_3 = MEM$
 (4) $R_1 = COC_6H_5 \quad R_2 = R_3 = H$
 (5) $R_1 = COC_6H_5 \quad R_2 = H \quad R_3 = MEM$
 (6) $R_1 = R_2 = H \quad R_3 = MEM$
 (13) $R_1 = H \quad R_2 = R_3 = C_6H_5CH$
 (14) $R_1 = COC_6H_5 \quad R_2 = R_3 = C_6H_5CH$
 (15) $R_1 = COC_6H_5 \quad R_2 = \beta-D-Glc(Ac)_4 \quad R_3 = MEM$
 (16) $R_1 = COC_6H_5 \quad R_2 = \beta-D-Glc(Ac)_4 \quad R_3 = H$
 (17) $R_1 = COC_6H_5 \quad R_2 = R_3 = \beta-D-Glc(Ac)_4$



- (7) $R_1 = R_2 = R_3 = H$
 (8) $R_1 = Me \quad R_2 = R_3 = H$
 (9) $R_1 = Me \quad R_2 = H \quad R_3 = MBM$
 (10) $R_1 = COC_6H_5 \quad R_2 = R_3 = H$
 (11) $R_1 = COC_6H_5 \quad R_2 = H \quad R_3 = MEM$
 (12) $R_1 = R_2 = H \quad R_3 = MEM$

