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# A SYNTHETIC ROUTE TO α AND β-ANOMERS OF METHYL 2-DEOXY-D-RIBOFURANOSIDE

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Deoxy-ribose and its glycosides particularly the furanosides, are extremely useful in carbohydrate chemistry. α and β-anomers of methyl 2-deoxy-D-ribofuranoside (methyl 2-deoxy-D-erythropentofuranoside) can be synthesised directly from 2-deoxy-D-ribose. However, this method is used only on a small scale (< 1.0g.) as 2-deoxy-D-ribose is an expensive sugar. In this communication, a method is reported (applicable on a 30.0g. scale) to convert in high yield α and β methyl D-arabinofuranoside (2,9) (obtained from the more inexpensive arabinose) to α and β methyl 2-deoxy-D-ribofuranoside (8,13).

1,3-Dicholoro-1,1,3,3-tetraisopropyldisiloxane (1) a reagent[1,2] used in nucleoside chemistry was used simultaneously to protect 3 and 5 hydroxy functions of methyl α-D-arabinofuranoside (2). The resulting methyl 3,5,-O-(tetraisopropyldisiloxanyl)-α-D-arabinofuranoside(3,80%) was esterified with pivaloyl chloride to give the 2-pivaloate (4,85%) and with diphenyl phosphochloridate to give 2-dipenyl phosphate (5,90%) respectively. $^1$H n.m.r. spectra of these derivatives revealed that esterification had taken place at C-2 and hence in compound 3, the free hydroxyl was located at C-2. Thus simultaneous protection had been achieved at positions 3 and 5 of the arabinofuranoside. Compounds 3 was converted into the imidazolylthiocarbonyl derivative (6,94%) and reduced with n-tributyltinhydride[3,4] to yield the silylated 2-deoxy derivative (7,80%). Removal of the silyl groups with n-Bu$_4$NF gave in high yield methyl 2-deoxy α-D-ribofuranoside (8,95%). Similar treatment of methyl β-D-arabinofuranoside (9) by first selectively protecting the 3,5 hydroxyls (10,80%), followed by thioimidazolylation (11,92%), radical induced reductive cleavage (12,80%) and deprotection gave methyl 2-deoxy- β-D-ribofuranoside (13,95%). All compounds gave correct microanalyses and had $^1$H and $^{13}$C n.m.r spectra in accordance with the assigned structures.

References

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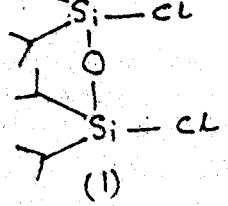
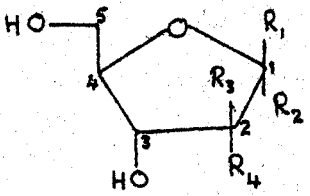
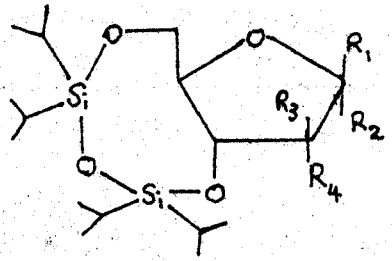
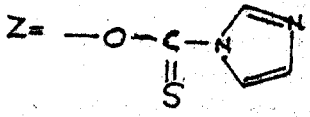


(1)





| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| (2) | H | OMe | OH | H |
| (8) | H | OMe | H | H |
| (9) | OMe | H | OH | H |
| (13) | OMe | H | H | H |



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| (3) | H | OMe | OH | |
| (4) | H | OMe | $OC(O)CMe_3$ | H |
| (5) | H | OMe | $OP(O)(OPh)_2$ | H |
| (6) | H | OMe | Z | H |
| (7) | H | OMe | H | H |
| (10) | OMe | H | OH | H |
| (11) | OMe | H | Z | H |
| (12) | OMe | H | H | H |