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Preliminary communication

Reaction of ethynylmagnesium bromide with 2,3-*O*-isopropylidene-D-ribose and 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose: syntheses of glycofuranosylethynes

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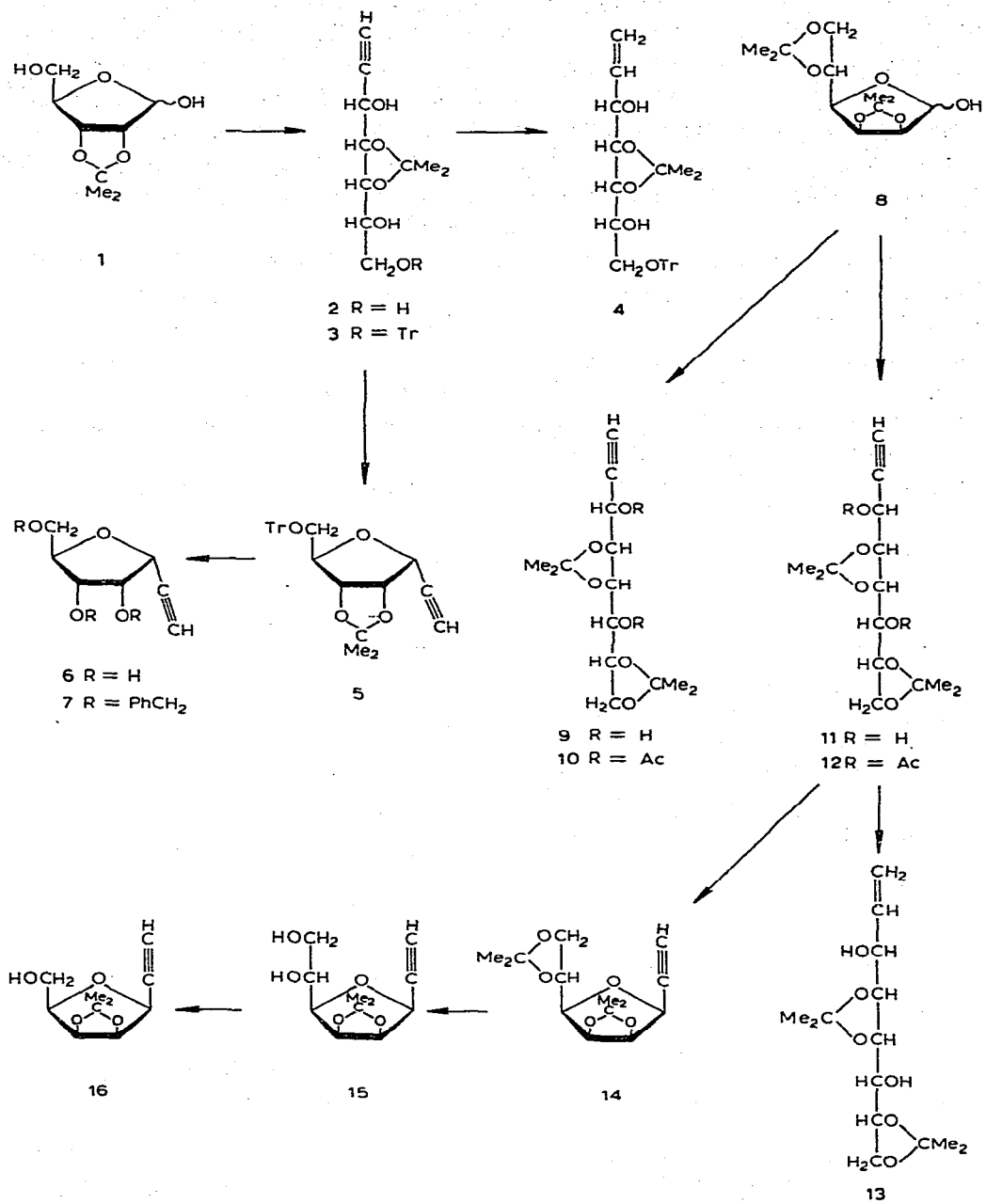
We have previously described[1] the synthesis of the potential *C*-nucleoside precursors, 2,3,5-tri-*O*-benzyl-β-D-ribofuranosylethyne and its α-D anomer, from 2,3,5-tri-*O*-benzyl-D-ribofuranose. In order to extend the range of protecting groups, we have now explored syntheses starting from 2,3-*O*-isopropylidene-D-ribose (**1**) and have encountered some interesting stereochemical results.

The isopropylidene compound, which probably exists[2] mainly as the furanose **1**, reacted with ethynylmagnesium bromide in tetrahydrofuran to give the crystalline D-*allo* triol **2**, m.p. 100–101°, $[\alpha]_D$ −63.6° (ethanol), in 70% yield. Tritylation of **2** in pyridine afforded the crystalline ether **3**, m.p. 122–122.5°, $[\alpha]_D$ +35.8° (chloroform). The D-*allo* configuration of **2** and **3** was established by reduction of **3** with lithium aluminium hydride[3] to give the crystalline alkene **4**, m.p. 153°, $[\alpha]_D$ +19.4° (chloroform); acidic hydrolysis of **4**, followed by ozonolysis[3,4] gave D-allose as the sole hexose product, identified chromatographically and by conversion (borohydride reduction) into crystalline allitol.

The D-*allo* configuration in **2** and **3** was unexpected since Chilton and his colleagues[5] had claimed that reaction of the mannofuranose **8** and ethynylmagnesium bromide gave mainly the D-*glycero*-D-*galacto* isomer **9**, isolated as the crystalline diacetate **10** in 68% yield. In **9**, C-3 and C-4 have a *threo* configuration, whereas in **2** the relationship is *erythro*. We have reinvestigated Chilton's system and have found that the major product, isolated as the diacetate (53%), m.p. 82.5–83°, $[\alpha]_D$ −11.7° (chloroform) (lit.[5] m.p. 80°), is not **10**, but is the D-*glycero*-D-*talo* isomer **12**. From the mother liquors, after deacetylation and chromatography, the diols **11**, m.p. 75–76°, $[\alpha]_D$ −31.6° (chloroform) (lit.[5] m.p. 74°), and **9**, m.p. 98–98.5°, $[\alpha]_D$ −21.5° (chloroform), were isolated in yields of 12 and 5%, respectively, making a total of 65% for **11** and **12**.

The D-*glycero*-D-*talo* configuration of **11** and **12** was shown by reduction[3,5] of **12** to the crystalline olefin **13**, m.p. 45–46°, $[\alpha]_D$ +0.9° (chloroform), which was hydrolysed



with acid and the product subjected to ozonolysis. D-*glycero*-D-*talo*-Heptose[6] was the only heptose detectable by paper chromatography; it was clearly distinguishable from D-*glycero*-D-*galacto*-heptose. In a separate experiment, the heptose was converted into crystalline D-*glycero*-D-*talo*-heptitol (D-volemitol)[7] by reduction with sodium borohydride. The earlier

assignment[5] depends on the isolation of a low yield (8%) of crystalline D-*glycero*-D-*galacto*-heptonolactone from a similar reaction sequence, but including oxidation with alkaline silver oxide, treatment which may have caused epimerisation at C-2 of the heptose moiety.

In the *ribo* series, ring closure of **3** by means of toluene-*p*-sulphonyl chloride in pyridine[1] afforded the amorphous α-D-ribosylethyne **5**, $[\alpha]_D$ −23.8° (chloroform), in 94% yield. Acidic hydrolysis of **5** gave crystalline α-D-ribofuranosylethyne (**6**), m.p. 102–102.5°, $[\alpha]_D$ +4.0° (ethanol), in 70% yield; the structure of **6** was confirmed by benzylation (sodium hydride/benzyl chloride[8]) to give the known[1] ether **7**.

In the *manno* series, ring closure of **11** in similar fashion gave (75%) the crystalline β-D-mannofuranosylethyne **14**, m.p. 113–114°, $[\alpha]_D$ +34.6° (chloroform), which could be converted into **15**, m.p. 92°, $[\alpha]_D$ +34.8° (chloroform), by partial acidic hydrolysis. Periodate oxidation of **15**, followed by reduction with borohydride, afforded the crystalline β-D-lyxofuranosylethyne **16**, m.p. 108–108.5°, $[\alpha]_D$ +33.3° (chloroform).

All new compounds gave satisfactory analytical and spectroscopic data. We thank Drs. H. S. Isbell, B. E. Stacey, and E. Zissis for the provision of several reference compounds, and the Science Research Council for a postgraduate studentship to A.D.D.

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