

6-Deoxy-D-galacto-heptose (V). The above di-*O*-isopropylidene derivative IV (39 mg) was treated with trifluoroacetic acid-water⁸ (9:1, 10 ml) at room temperature for 5 min. The solution was concentrated and the product dissolved in water, filtered and concentrated to a syrup (27 mg) $[\alpha]_D + 75^\circ$ (c 0.9, H₂O). An aliquot of the material was transformed into 6-deoxy-D-galacto-heptitol hexaacetate by reduction with sodium borohydride followed by acetylation.⁹ The GLC retention time relative to that of D-glucitol hexa-acetate (3 % ECNSS-M on Gas-Chrom Q at 180° and a flow rate of 30 ml/min) was 1.35. Another aliquot was reduced with sodium borodeuteride and then converted into the hexamethyl ether. The MS of the resulting 6-deoxy-1-deuterio-1,2,3,4,5,7-hexa-*O*-methyl-D-galacto-heptitol showed the following (primary) fragments: *m/e* 235, 191, 178, 147, 134, 103, 90, 46, and 45. The remainder of the spectrum was in accordance with the presumed structure. The above 6-deoxy-D-galacto-heptitol hexaacetate crystallized, m.p. 123–125°, $[\alpha]_D - 9^\circ$ (c 0.4, CHCl₃). (Found: C 50.7; H 6.29. C₁₉H₂₈O₁₂ requires: C 50.9; H 6.29).

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The Structure of Methyl β -D-Ribopyranoside

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X-Ray crystallographic studies on the pyranose form of aldopentoses^{1–6} have shown that the structures agree with those predicted by Reeves.⁷ Thus, β -arabinose,^{1–3} β -lyxose,⁴ and α -xylose,^{5,6} are found to have the conversion forms 1a2e3e4a, 1e2a3e4e, and 1a2e3e4e, respectively.

As regards the fourth aldopentose, ribose, preliminary crystallographic data only have been reported.⁸ However, a structure study of 2-deoxy- β -ribose has been carried out.⁹

The conversion form 1a3e4a which 2-deoxy- β -ribose has in the crystalline state, does not agree with Reeves' predictions, and it has been proposed in this connection that an axial substituent on C(1) should be regarded as an element of stability rather than an element of instability.⁹ An X-ray structure study of methyl β -ribopyranoside which may occur as 1a2a3e4a or 1e2e3a4e, was therefore thought of interest.

The results from this study show, cf. Fig. 1, that methyl β -D-ribopyranoside in the crystalline state has the conversion form 1a2a3e4a, which from Reeves' stability scheme⁷ is supposed to be the least stable one.

One may query, however, whether the assumed stabilizing effect of the 1a substituent has been decisive for the structure in this case. There is namely an intramolecular hydrogen bond between O(2) and O(4) which at least to some degree stabilizes the molecule. Similar intramolecular hydrogen bonds occur in methyl 1-thio- β -D-ribopyranoside and methyl 1,5-dithio- β -D-ribopyranoside,¹⁰ and the possibility for such bonding should therefore be taken into account when judging about the stability of the conversion forms of pyranoses. It should be mentioned in this connection that methyl 5-thio- β -D-ribopyranoside occurs as 1e2e3a4e in the crystalline state.¹¹

The C–O and C–C bond lengths in methyl β -D-ribopyranoside, as derived from the coordinates in Table 1, are shown in Fig. 1. The values agree with those reported by James and Stevens from an independent X-ray study of the compound,¹² and also with those previously reported for glycoside structures.^{13,14}

The three hydroxyl hydrogens participate in hydrogen bonds. They are, O(2)...O(4) = 2.77 Å with H(O2)...O(4) = 2.09 Å, O(3)...O(2)' = 2.85 Å with H(O3)...O(2)' = 2.03 Å, and O(4)...O(3)' = 2.87 Å with H(O4)...O(3)' = 2.22 Å. Thus each of the hydroxyl oxygens donates as well as accepts a hydrogen bond.

Methyl β -D-ribopyranoside crystallizes from ethyl acetate,¹⁵ as orthorhombic prisms elongated along the c-axis.

Table 1. Atomic coordinates in fractions of corresponding cell edges. Standard deviations, referring to last digits, are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-0.2423(11)	0.35556(31)	0.5762(11)
C(2)	-0.2066(10)	0.42624(30)	0.4870(11)
C(3)	0.0068(11)	0.45093(32)	0.5691(13)
C(4)	0.1735(11)	0.40168(34)	0.5023(14)
C(5)	0.1177(14)	0.33432(38)	0.5942(18)
C(6)	-0.3515(18)	0.30015(18)	0.9149(18)
O(1)	-0.2778(9)	0.35935(23)	0.8146(8)
O(2)	-0.2255(9)	0.42778(24)	0.2445(9)
O(3)	0.0569(7)	0.51497(20)	0.4822(9)
O(4)	0.1937(9)	0.39510(27)	0.2554(11)
O(5)	-0.0808(7)	0.31181(19)	0.5150(8)
H(11)	-0.358(11)	0.334(3)	0.491(11)
H(21)	-0.317(9)	0.455(3)	0.578(11)
H(31)	-0.018(8)	0.452(2)	0.733(10)
H(41)	0.295(9)	0.419(3)	0.579(10)
H(51)	0.123(13)	0.338(3)	0.754(13)
H(52)	0.217(10)	0.299(3)	0.544(11)
H(61)	-0.453(13)	0.310(3)	1.025(14)
H(62)	-0.254(15)	0.279(4)	1.005(20)
H(63)	-0.408(16)	0.269(5)	0.858(17)
H(O2)	-0.126(13)	0.407(4)	0.204(15)
H(O3)	-0.037(10)	0.542(3)	0.559(11)
H(O4)	0.222(11)	0.426(3)	0.196(13)

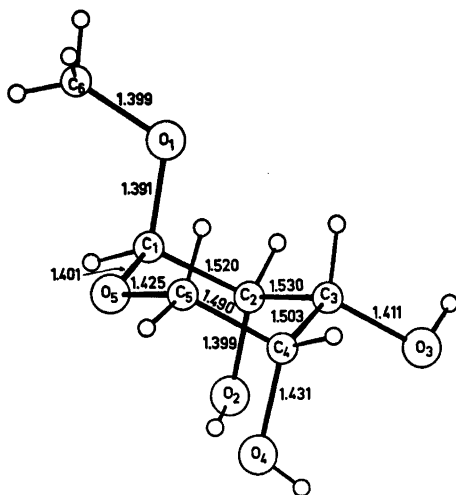


Fig. 1. The methyl β -D-ribose molecule with C—C and C—O bond lengths. The standard deviations are 0.009–0.011 Å for the C—C bonds and 0.008–0.011 Å for the C—O bonds.

gated along the *c*-axis. The crystals belong to the space group $P2_12_12_1$ with $Z=4$.

Unit cell dimensions were determined by measuring the 2θ settings for eight reflections on a Picker four-angle automatic diffractometer, with $\text{CuK}\beta$ radiation ($\lambda=1.39217$ Å). From a least squares treatment, the cell dimensions are, $a=6.415(2)$ Å, $b=19.994(3)$ Å, and $c=5.747(2)$ Å. The calculated density is 1.479 g/cm³, as compared with the density 1.48 g/cm³ found by flotation.

Intensity data were collected on the diffractometer, using $\text{CuK}\alpha$ radiation and omega scan. 660 reflections, measured within $\sin \theta = 0.865$, were reduced to structure factors in the usual way. The crystal used for data collection had the dimensions $0.2 \times 0.2 \times 0.4$ mm in the three axial directions. Absorption corrections were not applied.

The structure was solved by direct methods¹⁶ and refined by full matrix least squares to a final *R* factor of 0.07. The scattering factors used for oxygen and carbon were those given in *International Tables*.¹⁷ For hydrogen the scattering factor curve given by Stewart *et al.*¹⁸ was used.

Final atomic coordinates are listed in Table 1. The final list of structure factors is available on request.

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Electroorganic Preparations. XXXVI. Stepwise Reduction of Benzotrifluoride

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Electrochemical reduction of trifluoromethyl compounds has been observed in some instances.¹⁻⁴ In most cases reported the reduction has been performed in protic solvents, and under these conditions a complete reduction involving 6 F/mol to a methyl group is generally observed;¹⁻³ the only exception seems to be the reduction of 2,2,2-trifluoroacetophenone to acetophenone in 80 % aqueous ethanol during which monofluoroacetophenone was detected as an intermediate.³

In *N,N*-dimethylformamide (DMF) some trifluoromethylbenzenesulphonamides have been investigated polarographically⁴ and a stepwise reduction was found in some cases; the electrode reaction corresponded to a reductive cleavage of the carbon-sulphur bonds, and the resulting benzotrifluoride was reported to give a single polarographic wave.

In the present work the electrochemical behaviour of benzotrifluoride and some other α -halogenated toluenes have been investigated by means of cyclic voltammetry (CV) and controlled potential electrolysis (CPE).

Results and discussion. In Table 1 are given the peak potentials of benzotrifluoride (I), α,α -difluorotoluene (II), α -fluorotoluene (III), benzotrichloride (IV), α,α -dichloro- α -fluorotoluene (V), α -chloro- α,α -difluorotoluene (VI), benzal chloride (VII), α -chloro- α -fluorotoluene (VIII), and

benzyl chloride (IX). None of the electrode reactions are reversible on CV.

Whereas the peak potentials of II and III are very nearly equal, the potential of I is more than 200 mV less negative than that of II, and a reduction of I to II should be possible with a reasonable selectivity. The half-peak potential of II is about 0.05 V less negative than that of III which might indicate that the signal from II is a composite wave due to poorly separated peaks of the reduction of II to III and III to toluene. A reduction of II to III would thus be expected to be less selective than a reduction of I to II.

Cyclic voltammograms of I in DMF with added water showed that the peak potentials of the first and second peak were not affected by addition of up to 2 % of water. The background current raised and at a water content higher than about 2 % the waves merged with the background current.

The difference in reduction potential between that of the carbon-chlorine bond and that of the carbon-fluorine bonds in VI is about 0.7 V, sufficiently for a selective reduction; this was confirmed by a preparative reduction of VI to II in good yield. The potential difference between the reduction of the first and second carbon-chlorine bond in V is about 0.4 V; a selective reduction of V to VIII was shown to be possible.

The reduction of I was investigated in more detail; in Fig. 1 is shown the dependence of the concentrations of I, II, III, and toluene (X) on the electron consumption. The samples with-

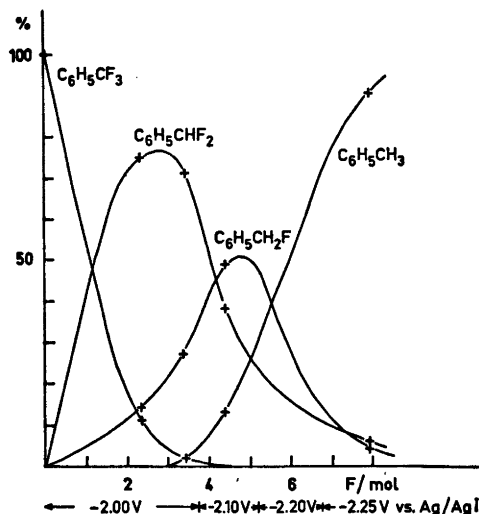


Fig. 1. Dependence on concentration of benzotrifluoride (I), α,α -difluorotoluene (II), α -fluorotoluene (III), and toluene (X) on electron consumption during electrolytic reduction of I in DMF containing tetrabutylammonium iodide.