The Two 1,4:3,6-Dianhydro-D-hexopyranoses

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WE report the isolation from the vacuum-pyrolysis products of both amylose and 3,6-anhydro-D-glucose of 1,4 : 3,6-dianhydro-D-glucopyranose (I), first obtained by gasification of wood.[1] The previously unknown epimer, 1,4 : 3,6-dianhydro-D-mannopyranose (II), has been similarly prepared in small yield from D-mannose. Their structures are assigned on the basis of proton magnetic resonance spectra.

TABLE 1. *Proton chemical shifts* (τ *values*) *at* 60 *Mc./sec.*

Compound	H–1	H–2	H–3	H–4	H–5	H–6 (two protons)
(I)	4·47	6·25	5·84	4·63	5·69	6·02
(II)	4·54	6·20	5·84	4·60	5·63	6·06

TABLE 2. *Proton coupling constants* (*c./sec.*) *at* 60 *Mc./sec. and dihedral angles.**

Compound	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6_1}$	$J_{5,6_2}$
(I)	<0·4 (75°)	1·0	<0·4 (105°)	4·5 (25°)	3·0 (40°)	1—2 (70°)	1—2 (50°)
(II)	2·0 (45°)	<0·4	6·5 (15°)	4·5 (25°)	3·0 (40°)	1—2 (70°)	1—2 (50°)

* Estimated from Cenco–Petersen models.

Crystallisation, from acetone, of the pyrolytic distillate from amylose[2] removed most of the lævoglucosan and left a syrup. Elution with water of a carbon-column chromatogram of the benzene–soluble fraction of this product gave, after the 1,6-anhydroglucoses, a dextrorotatory syrup which slowly solidified. Crystallisation of the solid from diethyl ether–light petroleum (b.p. 60—80°) gave the glucose derivative (I), m.p. 122—123° (lit.,[1] m.p. 127—128°). A benzene extract of the distillate from 3,6-anhydro-D-glucose, freed from carbonyl compounds by treatment with Amberlite IRA-400 resin in the bisulphite form, gave the same derivative. Gas–liquid chromatography of the trimethylsilyl ether of compound (I) gave one major peak with one-third the retention volume of 2,3,4-tri-(*O*-trimethylsilyl)lævoglucosan. Yields of the dianhydro-sugar from amylose (1·26%) and from 3,6-anhydro-D-glucose (34·8%) were estimated by direct g.l.c. of trimethylsilylated pyrolysis products.

A benzene extract of the pyrolysis products from D-mannose on carbon-column chromatography gave 1,4 : 3,6-dianhydro-D-mannopyranose, readily distinguished from the epimer (I) by infrared spectroscopy. The yield was 2·3% (by g.l.c.) A small amount was obtained crystalline, m.p. 105—110°. The trimethylsilyl ether of compound (II) had a very similar retention volume to that of the dianhydroglucose derivative.

The p.m.r. spectra of compounds (I) and (II) were measured on solutions in deuterium oxide at 60 Mc./sec. and the assignments in Tables 1 and 2 confirmed by examination at 100 Mc./sec. with the technique of double irradiation.

The ring protons show an unusually wide range of chemical shifts; in particular, the H-4 and H-1 (acetal) signals almost coincide. This effect, and the low values for coupling constants in relation to dihedral angles (*cf.* ref. 3) are probably attributable to ring strain. The best fit with the observed coupling constants is obtained with a conformation such that the 3,6-anhydro-ring has an 'envelope' conformation with C-5 displaced from the plane containing the other four ring atoms. This accounts satisfactorily for the inequality of $J_{3,4}$ and $J_{4,5}$, low values of $J_{5,6}$, and equivalence of the two

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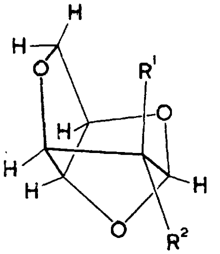
[1] D. Tischenko and N. Nosova, *Zhur. obshchei Khim.*, **1948**, **18**, 1193.

[2] R. B. Ward, in 'Methods in Carbohydrate Chemistry', Vol. II, ed. R. L. Whistler and M. L. Wolfrom, Academic Press, New York, 1963, p. 394.

C-6 protons, in contrast to the near equality of $J_{3,4}$ and $J_{4,5}$, high $J_{5,6}$ values, and non-equivalence of the C-6 protons quoted for 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose[3] in which the 3,6-anhydro-ring assumes a different conformation. The spectrum of compound (II) differs significantly from that of compound (I) in the values of $J_{1,2}$ and $J_{2,3}$, and is consistent with a C-2 epimer of similar conformation. The long-range coupling constant $J_{1,3}$ for the glucose derivative (I) resembles $J_{1,3}$ for some 1,6-anhydro-β-D-hexopyranose triacetates[4] rather than $J_{2,6}$ and $J_{3,5}$ for the structurally related bornane-2,3-*endo*-diol.[5]



(I); $R^1 = H$, $R^2 = OH$

(II); $R^1 = OH$, $R^2 = H$

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[3] R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLauchlan, *J. Chem. Soc.*, 1962, 3699.

[4] L. D. Hall and L. Hough, *Proc. Chem. Soc.*, 1962, 382.

[5] F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 789.