

Note

Synthesis of β -D-glucopyranosides of acetylenic alcohols

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A series of tetra-*O*-acetyl- β -D-glucopyranosides of mono- and di-acetylenic alcohols (Table I) has been obtained by the reaction of tetra-*O*-acetyl- α -D-glucopyranosyl bromide¹ with the appropriate alcohol. Deacetylation with sodium methoxide² of some of the acetates afforded the corresponding β -D-glucopyranosides (Table II).

Under the alkaline conditions used for deacetylation, nucleophilic attack of OH-2 on the acetylenic bond is possible. A signal for an acetylenic proton, however, could be observed in the n.m.r. spectrum of 2-propynyl β -D-glucopyranoside, and re-acetylation yielded the parent tetra-acetate.

EXPERIMENTAL

The tetra-*O*-acetyl- β -D-glucopyranosides were prepared by using mercuric salts as catalyst and acetonitrile as solvent, according to the method described by Helferich³⁻⁵, and were crystallised from methanol. The β -D-glucosides were purified by chromatography on silica gel with methanol as eluent; 2-propynyl β -D-glucopyranoside crystallised as a hemi-hydrate.

I.r., n.m.r., and mass spectra are in agreement with the expected structures. The melting points were determined with a Kofler hot-stage apparatus. The optical rotations were measured with a 0.05° Zeiss polarimeter.

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TABLE I
ACETYLATED β -D-GLUCOPYRANOSIDES

Alcohol	Yield (%)	M.p. (degrees)	[α] _D ²⁰ (degrees) ^a	Found (%)		Formula	Calc (%)	
				C	H		C	H
Prop-2-yn-1-ol	50	118-119	-50.5	52.7	5.7	C ₁₇ H ₂₂ O ₁₀	52.8	5.7
Pent-1-yn-3-ol	34	107-108	-12.2	54.5	6.3	C ₁₉ H ₂₆ O ₁₀	55.0	6.3
4-Methylpent-1-yn-3-ol	20	124-125	-25.4	56.0	6.5	C ₂₀ H ₂₈ O ₁₀	56.0	6.6
1-Phenylprop-2-yn-1-ol	27	124-126	-39.4	59.3	5.5	C ₂₃ H ₂₆ O ₁₀	59.7	5.6
3-Ethylpent-1-yn-3-ol	30	89-89.5	+6.1	56.6	6.9	C ₂₁ H ₃₀ O ₁₀	57.0	6.9
Hex-4-en-1-yn-3-ol	25	108.5-109	+30.2	56.4	6.1	C ₂₀ H ₂₈ O ₁₀	56.3	6.1
2-Methylhepta-4,6-diyn-3-ol	19	106-108				C ₂₂ H ₂₈ O ₁₀	58.4	6.2
2,7-Dimethyl-4-octyne-3,6-diol	44	145-146	-15.8	56.0	6.6	C ₃₈ H ₅₄ O ₂₀	56.1	6.5
But-3-yn-1-ol	57	136-137	-21.59	53.8	6.1	C ₁₈ H ₂₄ O ₁₀	54.0	6.0

^ac ~2, chloroform.

TABLE II
β-D-GLUCOPYRANOSIDES

Alcohol	Yield (%)	M.p. (degrees)	Solvent ^a	[α] _D ²⁰ (degrees) ^b	Found (%)		Formula	Calc. (%)	
					C	H		C	H
Prop-2-yn-1-ol	32	55-56	A	-51.3	47.6	6.6	C ₉ H ₁₄ O ₆ ·0.5 H ₂ O	47.6	6.6
Pent-1-yn-3-ol	67	108-108.5	A	-1.9	51.1	7.3	C ₁₁ H ₁₈ O ₆	53.6	7.3
4-Methylpent-1-yn-3-ol	74	141.5-142	A	+11.4	55.1	7.7	C ₁₂ H ₂₀ O ₆	55.3	7.7
1-Phenylprop-2-yn-1-ol	75	156-157	B	-46.3	61.0	6.2	C ₁₅ H ₁₈ O ₆	61.2	6.1
But-3-yn-1-ol	52	101-102	B	-28.1	50.1	7.0	C ₁₀ H ₁₆ O ₆	49.9	7.0

^aCrystallisation from A, methanol; and B, methanol-acetone (1:1). ^bc ~2, water.