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Note

Bis(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)amine obtained by a fusion reaction

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Under fusion conditions, glycosides can be formed by the elimination of acetic acid[1], trimethylsilyl halide[2], or trihalogenoacetic acid[3] from acylated sugars and aglycons.

We now report a novel fusion reaction, namely, the conversion of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylamine (**1**) into bis(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)amine (**2**) by the elimination of ammonia. Compound **2**, which was obtained crystalline (57%), was originally isolated[4] as a by-product in the preparation of **1**.

When the crude fusion product was eluted from Sephadex LH-20 with ethanol, **2** was obtained first, followed by maltose octa-acetate (reference added), and then 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucose. The n.m.r. spectrum of **2**

TABLE I

DATA ON TWO BIS(PER-*O*-ACETYLGLYCOSYL)AMINES

Compound[a]	*Yield* (%)	*M.p.*	$[\alpha]_D^{20}$ (c, *chloroform*)	R_F[b]	*Found* (%)		
					C	*H*	*N*
Bis(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)amine[c]	47	Amorphous	+59° (1.2)	0.72	49.64	5.84	1.84
Bis(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)amine[d]	18	222–224°	+86° (0.64)	0.70	49.59	5.81	2.00

[a]Calc. for $C_{28}H_{39}NO_{18}$: C, 49.63; H, 5.80; N, 2.07. [b]T.l.c., benzene–ethyl acetate (1:1). [c]Anomeric configuration not established; ν_{max}^{KBr} 3400 (NH), 1750, 1240 (C=O, C–O of OAc), and 1090–1010 cm^{-1} (C–O). N.m.r. data ($CDCl_3$): δ 5.32 (2 H), 5.2–4.9 (5 H), 4.3–3.7 (7 H), 3.00 (1 H, NH), 2.13, 2.00, 1.98, and 1.93 (24 H, 8 OAc). [d]ν_{max}^{KBr} 3400 (NH), 1750, 1250 (C=O, C–O of OAc), and 1100–1000 cm^{-1} (C–O). N.m.r. data ($CDCl_3$): δ 5.4–3.9 (14 H), 3.00 (1 H, NH), and 2.07–1.99 (24 H, 8 OAc); lit.[7]: α anomer, m.p. 216–217°, $[\alpha]_D$ +87° (chloroform); β anomer, m.p. 190–192°, $[\alpha]_D$ +7.6° (chloroform).

indicated the presence of three protons (NH) exchangeable with deuterium, and a ratio of intensities of acetyl and methine plus methylene protons of ~12:7 after the deuterium exchange. Compound **2** had i.r. bands for NAc and OAc groups, and the electron-impact and chemical-ionisation (NH_3) mass spectra contained signals for M^+ at *m/e* 675 and MH^+ at *m/e* 676, respectively.

Compound **2** was also obtained when zinc chloride was used as catalyst, but considerable degradation occurred when toluene-*p*-sulphonic acid was employed in this capacity.

Two other diglycosylamines were also prepared by the novel fusion procedure (Table I) from the corresponding glycosylamines.

EXPERIMENTAL

Mass spectra were recorded with a Shimadzu LKB-9000 mass spectrometer at an accelerating potential of 3,500 V, and a source temperature of 250° for electron impact (60 eV) and 230° for chemical ionisation (NH_3, 500 eV). The other methods have been described previously[6].

*Bis(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)amine* (**2**). — Compound **1** {228 mg, m.p. 156–157°, $[\alpha]_D^{20}$ −22° (*c* 0.5, chloroform)} was fused at ~160° for 5–10 min with the exclusion of moisture and under weak suction. A solution of the resulting, slightly brown syrup in ethanol (~20 ml) was decolorised with activated charcoal and concentrated *in vacuo* to give a syrup (207 mg, 93%) which crystallised from ethanol, to yield **2** (126 mg, 57%), m.p. and mixture m.p. 259–262° (dec.), $[\alpha]_D^{20}$ −27° (*c* 1.3, chloroform) {lit.[5] m.p. 260°, $[\alpha]_D$ −32° (*c* 2, chloroform); *cf.* m.p. 245–246°, $[\alpha]_D$ +44° (*c* 2, chloroform) for the αβ compounds[5]}; ν_{max}^{KBr} 3360 (NH), 1750 and 1250 (C=O and C–O of OAc), 1660 and 1540 (C=O and NH of NHAc), and ~1050 cm^{-1} (C–O). N.m.r. data ($CDCl_3$): δ 6.05 (d, 2 H, NH), 5.4–3.4 (14 H, -CH- and $-CH_2$), 2.15 (1 H, NH), 2.10, 2.00, and 1.95 (3 s, 15 H, 2 NAc, 5 OAc). Mass spectrum: *m/e* 675 (M^+), 616 (M — OAc), 556 (616 — AcOH), 496 (556 — AcOH), 436 (496 — AcOH), 330, 270 (330 — AcOH), 210 (270 — AcOH), and 150 (210 — AcOH). The ion *m/e* 330 is identical with that given by 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose[8].

Anal. Calc. for $C_{28}H_{41}N_3O_{16}$: C, 49.78; H, 6.12; N, 6.22. Found: C, 49.69; H, 6.08; N, 6.17.

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