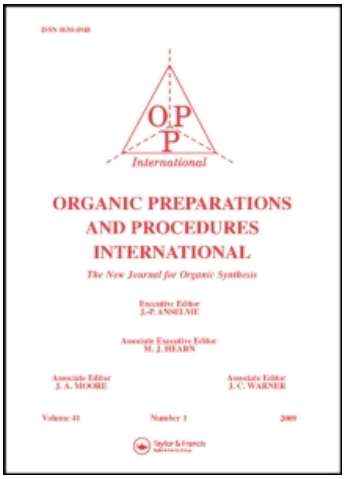

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HETEROCYCLIC DERIVATIVES FROM SUGARS VIII. PREPARATION OF 1-(N-METHYL-N-PHENYL)-AMINO-1-DEOXY ALDITOLS

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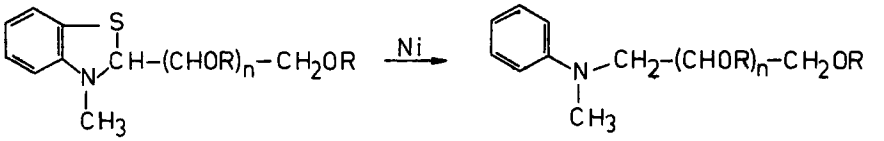
In the framework of synthetic and structural studies of heterocyclic derivatives of sugars in our laboratory,[1] the desulfurisation of some polyhydroxyalkyl benzothiazolines[2] and thiazolidine carboxylic acids[3] was performed. We now report on the preparation of some 1-(N-methyl-N-phenyl)-amino-1-deoxy alditols via desulfurisation of the corresponding 2-tetrahydroxybutyl-3-methyl- or 2-pentahydroxypentyl-3-methyl benzothiazolines[1c] or their acetates[1c] with Raney nickel.



R=H, Ac n=3,4

N-substituted glycamines usually are prepared either by high pressure hydrogenation of N-glycosides or by reduction of 1-alkylamino- or 1-arylamino ketoses formed in the Amadori rearrangement or by N-substitution of glycamines.[4] Hydrogena-

tion of N-glycosides of secondary amines is complicated,[6] although Kuhn and Birkofer[7] were able to obtain N-1'-sorbityl piperidine by this way. 1-(N-methyl-N-phenyl)-amino-1-deoxy-D-glucitol was prepared by Karrer and Salomon[5] through the reaction of N-phenyl-D-glucamine with monochloracetic acid and decarboxylation of the reaction product. Our method is simple and convenient for the preparation of N-methyl-N-phenyl glycamines and avoids high pressure hydrogenation.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Kofler block. IR spectra were obtained with a Unicam SP 200 spectrophotometer on potassium bromide discs. NMR spectra were recorded with a JEOL MH-100 instrument. Optical rotations were determined with a Schmidt-Haensch polarimeter.

Typical procedure.-

1-(N-methyl-N-phenyl)-amino-1-deoxy-D-glucitol.-

a.) 2-(D-Gluco-pentahydroxypentyl)-3-methyl benzothiazoline[1c] (2.0 g., epimeric mixture) in 250 ml of ethanol was refluxed with 30 g of Raney nickel for 5 hours on a steam bath. After filtration of the hot suspension the solvent was evaporated under diminished pressure and the residue was crystallized from ethanol to give 1.49 g (72.2%), mp. 140°, lit.[5] 150°, $[\alpha]_D^{23}$ = 3.4° (c. 1.16, methanol)

Anal. Calcd. for $C_{13}H_{21}NO_5$: C, 57.92, H, 7.77, N, 5.16
Found: C, 57.75, H, 7.74, N, 5.45

IR spectrum: 3463, 3378, 3270 cm^{-1} (ν as O-H), 2974 (ν s CH_3),

1511 (monosubst. aryl), 1207 (ν C-N), 1093, 1068, 1039 (ν C-O); NMR (DMSO-d_6): δ6.4-7.2 (5 proton multiplet, phenyl), δ2.86 (3 proton singlet, CH_3), δ3.3-3.8 (8 proton multiplet, CH_2 + CH of the sugar chain).

b.) This compound was obtained also from the desulfurisation product of 2-(D-gluco-pentaacetoxypentyl)-3-methylbenzothiazoline by Zemplén's saponification method.[8] The compounds obtained in a.) and b.) were identical by mixture melting point. The following compounds were obtained in a same way, with only the solvents or times being changed.

1-(N-methyl-N-phenyl)-amino-1-deoxy-D-ribitol.- In EtOH, 6 h. Yield: 56.5%, mp. 100-101°, $[\alpha]_D^{23}$ = -48° (c. 1.5, methanol).

Anal. Calcd. for $C_{12}H_{19}NO_4$: C, 59.73, H, 7.93, N, 5.80
Found: C, 59.72, H, 7.78, N, 5.38

1-(N-methyl-N-phenyl)-amino-1-deoxy-D-arabinitol.- In EtOH, 8.5 h. Yield: 60%, mp. 150-160°, $[\alpha]_D^{23}$ = -7.8° (c. 1.5, methanol).

Anal. Calcd. for $C_{12}H_{19}NO_4$: C, 59.73, H, 7.93, N, 5.80
Found: C, 59.54, H, 7.93, N, 5.93

1-(N-methyl-N-phenyl)-amino-1-deoxy-L-arabinitol.- In EtOH, 6 h. Yield: 51.8%, mp. 154-156°, $[\alpha]_D^{23}$ = 8.1° (c. 1.5, methanol).

Anal. Calcd. for $C_{12}H_{19}NO_4$: C, 59.73, H, 7.93, N, 5.80
Found: C, 59.71, H, 7.93, N, 5.81

1-(N-methyl-N-phenyl)-amino-1-deoxy-2,3,4,5,6-penta-O-acetyl-D-glucitol.- In benzene, 6 h. Yield: 48.9%, mp. 82°, $[\alpha]_D^{23}$ = 22.3° (c. 2.2, acetone).

Anal. Calcd. for $C_{23}H_{31}NO_{10}$: C, 57.38, H, 6.48
Found: C, 57.39, H, 6.43

1-(N-methyl-N-phenyl)-amino-1-deoxy-D-galactitol.- In EtOH, 6 h. Yield: 72%, mp. 140°, $[\alpha]_D^{23}$= 5.8° (c. 1.54, methanol).

Anal. Calcd. for $C_{13}H_{21}NO_5$: C, 57.92, H, 7.77, N, 5.16
Found: C, 57.81, H, 7.78, N, 5.26

1-(N-methyl-N-phenyl)-amino-1-deoxy-2,3,4,5,6-penta-O-acetyl-D-galactitol.- Yield: 43%, mp. 128-130°, $[\alpha]_D^{23}$ = 16.2° (c. 1.5, methanol).

Anal. Calcd. for $C_{23}H_{31}NO_{10}$: C, 57.38, H, 6.48, N, 2.99
Found: C, 57.26, H, 6.47, N, 3.30

1-(N-methyl-N-phenyl)-amino-1-deoxy-D-mannitol.- Yield 79%, mp. 138-139°, $[\alpha]_D^{23}$ = 56° (c. 0.4, acetone).

Anal. Calcd. for $C_{13}H_{21}NO_5$: C, 57.92, H, 7.77
Found: C, 57.77, H, 7.73

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