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SYNTHESIS OF 1-ARYL-(GLYCOFURANO)IMIDAZOLIDINE-2-THIONES FROM NEW 2-(ALKYLAMINO)-2-DEOXYHEXOSES

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ABSTRACT

The new amino sugars 2-deoxy-2-(ethylamino)-α-L-glucopyranose, 2-deoxy-2-(propylamino)-α-L-glucopyranose, and 2-deoxy-2-(ethylamino)-α(or β)-L-mannopyranose have been prepared from L-arabinose by the aminonitrile synthesis. The reaction between these aminohexoses and aryl isothiocyanates affords the corresponding 3-alkyl-1-aryl-(1,2-dideoxy-α-L-glucofurano)[2,1-*d*]imidazolidine-2-thiones and 3-alkyl-1-aryl-(1,2-dideoxy-β-L-mannofurano)[2,1-*d*]imidazolidine-2-thiones. The structures of the new compounds described were elucidated by chemical and physical methods.

INTRODUCTION

The aminonitrile synthesis[1] constitutes a general method for preparing aminoaldoses from aldoses, and it has been widely applied to the preparation of pentosamines[2], hexosamines[3–9], and heptosamines[3,10,11]. During the past few years, we have used amino sugars in the preparation of new analogs of *C*-nucleosides of imidazole[12–14] *via* 1-aryl-(glycofurano)imidazolidine-2-thiones. We now report the application of the aminonitrile synthesis to the preparation of three new 2-alkylamino-2-deoxyhexoses (**9**, **11**, and **14**), and their reactions with aryl isothiocyanates, to afford the 1-aryl-(glycofurano)imidazolidine-2-thiones **15**, **17**, **19**, **21**, and **23**, which can be converted into acyclic *C*-glycosylimidazolines by acid-catalyzed isomerization[12].

RESULTS AND DISCUSSION

Treatment of L-arabinose with ethylamine in absolute methanol gave crystal-

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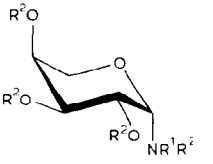
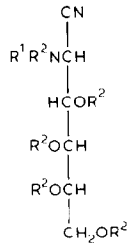
line *N*-ethyl-β-L-arabinopyranosylamine (**1**) in good yield; this was treated with HCN at 0–5°, to afford 2-deoxy-2-(ethylamino)-L-glucononitrile (**4**). Its epimer (**8**), having the L-*manno* configuration, was obtained by heating an ethanolic solution of **4** under reflux. The configuration of C-2 of both compounds was assigned on the basis of the structures of the amino sugars prepared from them, namely, **9** and **14**, whose C-2 configurations were demonstrated as described later. The rotatory power of these compounds are in agreement with generalized rules[15,16] enunciated for such other acyclic compounds as sugar nitriles, amides, hydrazides, and (alditol-1-yl)-heterocycles, being negative for **4** (L-*gluco* configuration) and positive for **8** (L-*manno* configuration). A review of the literature on sugar 2-aminonitriles[2–8,17–24] demonstrated the generality of those rules for these compounds. Similar treatment of the glycosylamine **2** with hydrogen cyanide gave 2-deoxy-2-(propylamino)-L-glucononitrile (**6**) whose C-2 configuration was demonstrated as indicated for **4** and **8**. The structures of these compounds are also in agreement with their elemental analyses, and their i.r. spectra, which showed the characteristic C≡N absorption band at 2220 cm^{-1}. The structures of **4** and **6** were also supported by the preparation and properties of their pentaacetates (**5** and **7**).



1 R^1 = Et, R^2 = H
2 R^1 = Pr, R^2 = H
3 R^1 = Pr, R^2 = Ac



4 R^1 = Et, R^2 = H
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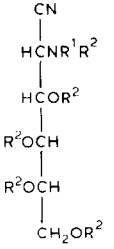

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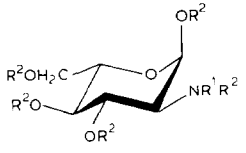
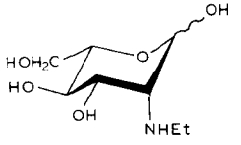


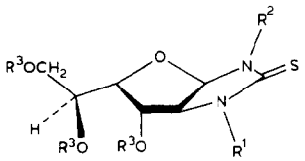
9 R^1 = Et, R^2 = H
10 R^1 = Et, R^2 = Bz
11 R^1 = Pr, R^2 = H
12 R^1 = Pr, R^2 = Ac
13 R^1 = Pr, R^2 = Bz



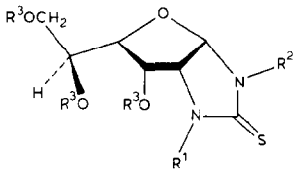
14

Controlled hydrogenation of the aminonitriles **4, 6,** and **8** by the method of Kuhn and Kirschenlohr[3,7,24] gave the 2-(alkylamino)-2-deoxy sugars **9, 11,** and **14**, respectively. The p.m.r. spectrum of **9** in D_2O–CF_3CO_2H showed two doublet signals, at 5.62 (J 3.3 Hz) and 5.17 p.p.m. (J 8.3 Hz), that could be readily assigned to H-1 of the α and β anomers, respectively. The value of 8.3 Hz is indicative of a *trans*-diaxial disposition of H-1 and H-2, and it is clear evidence of the L-*gluco* configuration in the $^1C_4$(L) conformation. The L-*gluco* configuration of **9** and **11** was also demonstrated from the p.m.r. spectra of their pentabenzoates (**10** and **13**), which showed large values (~8–11 Hz) for the coupling constants between H-2, H-3, H-4, and H-5, in agreement with the L-*gluco* configuration and the $^1C_4$(L) conformation. The α-anomeric configurations of **10** and **13** were deduced from their small $J_{1,2}$ values (~3 Hz). The α-anomeric configurations of the free amino sugars **4** and **6** were assigned from their mutarotations to more-positive values[25]. Hydrogenation of **8** afforded **14** in good yield as an amorphous and very hygroscopic powder whose structural assignation is based on the preparation of **21–24**, as described in the following paragraphs.

The reaction of amino sugars with aryl isothiocyanates yields 1-aryl-(1,2-dideoxy-glycofurano)[2,1-*d*]imidazolidine-2-thiones, which are useful intermediates in the synthesis of imidazole derivatives having interesting biological activities[12]. In this way, by reaction between the amino sugars **9, 11,** and **14** and aryl isothiocyanates, the imidazolidine-2-thiones **15, 17, 19, 21,** and **23** were obtained. The structures of these compounds were proved by elemental analyses, spectral data (u.v. and i.r.), and periodate oxidation of the glycofuranose ring.



15 R^1 = Et, R^2 = Ph, R^3 = H
16 R^1 = Et, R^2 = Ph, R^3 = Ac
17 R^1 = Et, R^2 = p-BrC_6H_4, R^3 = H
18 R^1 = Et, R^2 = p-BrC_6H_4, R^3 = Ac
19 R^1 = Pr, R^2 = Ph, R^3 = H
20 R^1 = Pr, R^2 = Ph, R^3 = Ac



21 R^1 = Et, R^2 = Ph, R^3 = H
22 R^1 = Et, R^2 = Ph, R^3 = Ac
23 R^1 = Et, R^2 = p-BrC_6H_4, R^3 = H
24 R^1 = Et, R^2 = p-BrC_6H_4, R^3 = Ac

Acetylation of these compounds gave the corresponding tri-*O*-acetyl derivatives **16, 18, 20, 22,** and **24**, whose p.m.r. spectra are shown in Table I. Complete sets of spin-coupling constants were determined in the presence of Eu(fod)$_3$; values for the unperturbed chemical-shifts were estimated by extrapolation back to zero concentration of Eu(fod)$_3$. The $J_{2',3'}$ values of **16, 18,** and **20** (0.0 Hz) are in good agreement with those reported[13,26–29] for other bicyclic compounds having similar structures, which show $J_{2',3'}$ ~0 Hz if H-2′ and H-3′ are in *trans* orientation,

TABLE I

^{1}H-N.M.R. DATA[a] (90 MHz) FOR **16, 18, 20, 22,** AND **24**

Compound No.	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6'*	*H-6''*	*OAc*	*Aryl*	*Et*	*Pr*
16	5.95 d $J_{1',2'}$ 6.7	4.36 d $J_{2',3'}$ 0.0	5.38 d $J_{3',4'}$ 3.0	4.28 dd[b] $J_{4',5'}$ 9.3	5.31 m[b] $J_{5',6'}$ 2.3 $J_{5',6''}$ 4.5	4.57 dd $J_{6',6''}$ −12.3	4.13 dd	2.11 s (3 H) 2.07 s (3 H) 2.03 s (3 H)	7.40 s	4.40–4.00 m (1 H) 3.53 m (1 H) 1.29 t (3 H)	
18	5.93 d $J_{1',2'}$ 6.7	4.33 d $J_{2',3'}$ 0.0	5.38 d $J_{3',4'}$ 3.0	4.25 dd[b] $J_{4',5'}$ 9.3	5.42 m[b] $J_{5',6'}$ 2.3 $J_{5',6''}$ 4.5	4.58 dd $J_{6',6''}$ −12.3	4.13 dd	2.11 s (3 H) 2.06 s (3 H) 2.03 s (3 H)	7.45 q	4.40–4.00 m (1 H) 3.54 m (1 H) 1.30 t (3 H)	
20	5.94 d $J_{1',2'}$ 6.7	4.30 d $J_{2',3'}$ 0.0	5.39 d $J_{3',4'}$ 2.8	4.27 dd $J_{4',5'}$ 6.0	5.37 m $J_{5',6'}$ 2.3 $J_{5',6''}$ 4.8	4.57 dd $J_{6',6''}$ −12.2	4.13 dd	2.14 s (3 H) 2.10 s (3 H) 2.07 s (3 H)	7.42 s		4.40–4.00 m (1 H) 3.45 m (1 H) 1.80 m (2 H) 1.10 t (3 H)
22	5.80 d $J_{1',2'}$ 7.7	4.58 d $J_{2',3'}$ 5.3	5.71 dd $J_{3',4'}$ 3.2	4.18 dd $J_{4',5'}$ 9.0	5.28 m $J_{5',6'}$ 2.7 $J_{5',6''}$ 5.0	4.53 dd $J_{6',6''}$ −12.3	4.05 dd	2.10 s (3 H) 2.02 s (3 H) 2.00 s (3 H)	7.43 m	4.24 m (1 H) 2.99 m (1 H) 1.22 t (3 H)	
24	5.80 d $J_{1',2'}$ 7.7	4.58 dd $J_{2',3'}$ 5.3	5.73 dd $J_{3',4'}$ 3.2	4.19 dd $J_{4',5'}$ 9.0	5.28 m $J_{5',6'}$ 2.7 $J_{5',6''}$ 5.0	4.54 dd $J_{6',6''}$ −12.3	4.06 dd	2.09 s (3 H) 2.03 s (3 H) 2.01 s (3 H)	7.47 m	4.24 m (1 H) 2.99 m (1 H) 1.22 t (3 H)	

[a]Recorded in $CDCl_3$ at 35.5°; δ scale (internal Me_4Si); J in Hz, with assignments verified by selective proton-decoupling, and INDOR. [b]Values obtained by extrapolation back to zero concentration of Eu(fod)$_3$. [c]Single primes denote numbering of atoms on the sugar ring-atoms. Double primes are reserved for the labeling of the upfield proton (usually) of a methylene group. [d]Signal multiplicities: d, doublet; dd, double doublet; m, multiplet; q, quartet; s, singlet; t, triplet.

whereas the *cis* arrangement gives medium values of $J_{2',3'}$ (~5–7 Hz). Consequently, the $J_{2',3'}$ values of **22** and **24** (5.3 Hz) demonstrate the *cis* arrangement for these protons, in agreement with the L-*manno* configuration assigned to compounds **21–24** and to the parent amino sugar **14**.

By comparing the ϕ values calculated[30] from the values of $J_{1',2'}$, $J_{2',3'}$, and $J_{3',4'}$ shown in Table I with those obtained from models[31,32], it may be assumed that the most favored conformation of the furanoid ring is the $^4T_3$ for compounds having the L-*gluco* configuration (**16, 18,** and **20**), and an intermediate between the $^4T_3$ and E_3 conformations for compounds having the L-*manno* configuration (**22** and **24**).

EXPERIMENTAL

General methods. — Solutions were evaporated *in vacuo* at temperatures below 50°. Melting points were determined with a Gallenkamp apparatus, and are uncorrected. Optical rotations were measured at 22 ±4° with a Perkin–Elmer 141 polarimeter (10-cm, 5-mL cell). Paper chromatography was performed on Whatman No. 1 paper by the ascending technique, with 1:1:1 1-butanol–pyridine–water as the eluant and silver nitrate–sodium hydroxide as the indicator. T.l.c. was performed on silica gel GF_{254} (Merck) with 3:1 ethyl acetate–ethanol (solvent *A*) or 3:2 benzene–ether (solvent *B*), and detection with u.v. light or iodine vapor. The formic acid produced in the oxidation with sodium periodate was determined as previously described[33,34]. I.r. spectra (KBr discs) were recorded with a Perkin–Elmer 399 spectrophotometer, and u.v. spectra with a Pye-Unicam SP8-250 instrument. ^{1}H-N.m.r. spectra (90 MHz, internal Me_4Si or sodium 4,4-dimethyl-4-silapentane-1-sulfonate) were recorded with a Perkin–Elmer R-32 spectrometer, and coupling constants were measured directly from spectra recorded at 300-Hz sweep-width (temperature of the probe, 35.5°). Assignments were confirmed by double resonance (spin–spin decoupling and INDOR), and overlapping signals were gradually shifted and separated from one another by incremental addition of $Eu(fod)_3$.

N-*Ethyl-β*-L-*arabinopyranosylamine* (**1**). — To a suspension of L-arabinose (21.2 g, 0.14 mol) in abs. ethanol (60 mL) was added ethylamine (20 mL, 0.3 mol), and the mixture was stirred until dissolution occurred. Subsequently, the solution was evaporated under diminished pressure, and the resulting syrup was triturated with ether, to give a solid residue (23.2 g, 93%) which was purified by recrystallization from abs. ethanol; m.p. 90–92°, $[\alpha]_D$ +27°, $[\alpha]_{578}$ +28°, $[\alpha]_{546}$ +32°, $[\alpha]_{436}$ +52°, $[\alpha]_{365}$ +78° (*c* 1.0, 1:9 NH_4OH–H_2O); $[\alpha]_D$ +33°, $[\alpha]_{578}$ +34°, $[\alpha]_{546}$ +39°, $[\alpha]_{436}$ +63°, $[\alpha]_{365}$ +93° (*c* 1.0, 2.5M HCl); ν_{max} 3500–3100 (OH) and 3270 cm^{-1} (NH). The product decomposes after several hours at room temperature.

N-*Propyl-β*-L-*arabinopyranosylamine* (**2**). — To a suspension of L-arabinose (4.16 g, 27.7 mmol) in methanol (50 mL) was added propylamine (4.8 mL, 58 mmol); the mixture was stirred until dissolution occurred, and processed as de-

scribed for the preparation of **1**, to give a solid product (4.2 g, 88%) which was purified by recrystallization from methanol–ether; m.p. 70–71°, $[\alpha]_D$ +38°, $[\alpha]_{578}$ +44°, $[\alpha]_{546}$ +52°, $[\alpha]_{436}$ +86.5°, $[\alpha]_{365}$ +134° (*c* 0.5, 1:9 NH_4OH–H_2O); $[\alpha]_D$ +29°, $[\alpha]_{578}$ +30°, $[\alpha]_{546}$ +34°, $[\alpha]_{436}$ +55°, $[\alpha]_{365}$ +80° (*c* 0.5, 2.5M HCl); ν_{max} 3500–3100 (OH) and 3280 cm^{-1} (NH). The product decomposes after several hours at room temperature.

N-*Acetyl-2,3,4-tri*-O-*acetyl*-N-*propyl*-α-L-*arabinopyranosylamine* (**3**). — To a suspension of **2** (0.2 g, 1.3 mmol) in pyridine (1 mL) was added acetic anhydride (1 mL, 9.8 mmol), and the mixture was kept for 24 h at room temperature and then poured into ice–water (75 mL). The resulting, syrupy product was extracted into dichloromethane (3 × 30 mL), and the extracts were combined and successively washed with saturated $CuSO_4$ solution (2 × 30 mL) and water (4 × 30 mL), dried (anhydrous sodium sulfate), and evaporated under diminished pressure, to give a syrup that crystallized on addition of ethanol (yield 0.2 g, 46%); m.p. 134–135°, $[\alpha]_D$ +77°, $[\alpha]_{578}$ +81°, $[\alpha]_{546}$ +91.5°, $[\alpha]_{436}$ +155°, $[\alpha]_{365}$ +238° (*c* 0.5, chloroform); ν_{max} 1740 (C=O ester) and 1645 cm^{-1} (C=O amide).

Anal. Calc. for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.77; H, 7.20; N, 4.07.

2-Deoxy-2-(ethylamino)-L-*glucononitrile* (**4**). — *Method A*. To a solution of **1** (21.3 g, 0.12 mol) in abs. ethanol (80 mL) was added dry hydrogen cyanide (12 mL). After several min, crystallization began, and the mixture was kept for 1 h at room temperature and then for 12 h at 0°. The crystals were filtered off, successively washed with cold abs. ethanol and ether, and dried *in vacuo* over sodium hydroxide (19.7 g, 80%); m.p. 115–117°, $[\alpha]_D$ −25°, $[\alpha]_{578}$ −26°, $[\alpha]_{546}$ −29°, $[\alpha]_{436}$ −45°, $[\alpha]_{365}$ −61° (*c* 1.0, pyridine); ν_{max} 3500–3100 (OH, NH) and 2220 cm^{-1} (C≡N).

Anal. Calc. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.72. Found: C, 47.04; H, 8.07; N, 13.75.

Method B. To a suspension of L-arabinose (47.8 g, 0.32 mol) in abs. ethanol (200 mL) was added ethylamine (45 mL, 0.67 mol), and the mixture was stirred until dissolution occurred. The solution was then cooled to 0°, and dry hydrogen cyanide (35 mL) was added. After several min at room temperature, compound **4** crystallized out, and it was processed as described in method A (40 g, 61%).

3,4,5,6-Tetra-O-*acetyl-2-deoxy-2-(*N-*ethylacetamido)*-L-*glucononitrile* (**5**). — To a suspension of **4** (1.0 g, 5.0 mmol) in pyridine (3.0 mL) was added acetic anhydride (4.5 mL). After being kept for 24 h at 0°, the mixture was poured into ice–water (80 mL), and the acetate crystallized on scratching. Compound **5** was washed repeatedly with water (yield, 1.1 g, 54%), and recrystallized from 25% ethanol; m.p. 103–105°, $[\alpha]_D$ −49°, $[\alpha]_{578}$ −51°, $[\alpha]_{546}$ −58.5°, $[\alpha]_{436}$ −101°, $[\alpha]_{365}$ −160.5° (*c* 1.0, chloroform); ν_{max} 2240 (C≡N), 1755, 1740, and 1730 (C=O ester), and 1640 cm^{-1} (C=O amide); ^{1}H-n.m.r. data ($CDCl_3$): δ 5.70–5.30 (m, 3 H, H-1,2,3), 5.11 (m, 1 H, H-4, $J_{4,5}$ 3.3, $J_{4,5'}$ 5.0 Hz), 4.30 (dd, 1 H, H-5, $J_{5,5'}$ −12.3 Hz), 3.43 (q, 2 H, CH_2), 2.19 (s, 3 H, NAc), 2.11 (s, 3 H, OAc), 2.06 (s, 9 H, 3 OAc), and 1.32 (t, 3 H, CH_3).

Anal. Calc. for $C_{18}H_{26}N_2O_9$: C, 52.17; H, 6.32; N, 6.76. Found: C, 52.39; H, 6.54; N, 7.00.

2-Deoxy-2-(propylamino)-L-*gluconononitrile* (**6**). — *Method A.* A solution of **2** (1.1 g, 6.5 mmol) in methanol (10 mL) was treated with dry hydrogen cyanide (2 mL), and the mixture was processed as described for the preparation of **4**, to give a crystalline product (0.63 g, 44%). Recrystallized from ethanol, it gave colorless needles, m.p. 96–97°, $[\alpha]_D$ −16°, $[\alpha]_{578}$ −17°, $[\alpha]_{546}$ −19°, $[\alpha]_{436}$ −29°, $[\alpha]_{365}$ −40° (*c* 0.5, pyridine); ν_{max} 3500–3100 (OH, NH) and 2220 cm^{-1} (C≡N).

Anal. Calc. for $C_9H_{18}N_2O_4$: C, 49.53; H, 8.31; N, 12.83. Found: C, 49.54; H, 8.60; N, 13.20.

Method B. A suspension of L-arabinose (4.8 g, 30 mmol) in ethanol (50 mL) was treated with propylamine (4.9 mL, 60 mmol) and stirred until dissolution occurred. Dry hydrogen cyanide (5 mL) was then added, and the mixture was kept at 0°. Crude **6** was collected by filtration, and successively washed with cool abs. ethanol and ether (yield, 2.2 g, 32%).

3,4,5,6-Tetra-O-*acetyl-2-deoxy-2-(*N-*propylacetamido)*-L-*gluconononitrile* (**7**). — Acetylation of **6** (0.2 g, 0.9 mmol) as described for **5** gave **7**. Recrystallized from ethanol, it had m.p. 115–116°, $[\alpha]_D$ −48°, $[\alpha]_{578}$ −49°, $[\alpha]_{546}$ −55.5°, $[\alpha]_{436}$ −96°, $[\alpha]_{365}$ −154° (*c* 0.4, chloroform); ν_{max} 2240 (C≡N), 1755, 1750, and 1735 (C=O, ester), and 1655 cm^{-1} (C=O, amide).

Anal. Calc. for $C_{19}H_{28}N_2O_9$: C, 53.27; H, 6.59; N, 6.54. Found: C, 52.87; H, 6.74; N, 6.75.

2-Deoxy-(2-ethylamino)-L-*mannononitrile* (**8**). — A solution of **4** (1.0 g, 4.9 mmol) in abs. ethanol (4.5 mL) was boiled under reflux for 5 min. Subsequently, it was kept at room temperature, and the product began to crystallize; the suspension was cooled for several hours in a refrigerator, and the crystals (0.65 g, 65%) were filtered off, and washed with abs. ethanol. Recrystallized from abs. ethanol, it had m.p. 116-118°, $[\alpha]_D$ +12°, $[\alpha]_{578}$ +12°, $[\alpha]_{546}$ + 13°, $[\alpha]_{436}$ +23°, $[\alpha]_{365}$ +36° (*c* 1.0, pyridine); ν_{max} 3500–3100 (OH, NH) and 2220 cm^{-1} (C≡N).

Anal. Calc. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.72. Found: C, 47.01; H, 8.20; N, 13.83.

2-Deoxy-2-(ethylamino)-α-L-*glucopyranose hydrochloride* (**9**). — A solution of **4** (35 g, 0.17 mol) in M hydrochloric acid (450 mL) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% palladium-on-barium sulfate (21.5 g). Paper chromatography showed the formation of **9** (R_F 0.61) and, after six days, the spot for the nitrile (R_F 0.82) had almost disappeared. Then, the catalyst was filtered off, and the filtrate was concentrated until crystals of ammonium chloride appeared; these were filtered off, the filtrate was evaporated, and the syrupy residue was treated with ethanol, to give crystals of **9** that were collected by filtration, washed with cold abs. ethanol, and dried *in vacuo* over calcium chloride (yield, 19.4 g). Several crops of crystals (14.0 g) were obtained from the mother liquor by addition of ethanol (total yield, 33.4 g, 75%). An analytical sample was obtained by dissolution of the crude product (1 g) in hot abs.

ethanol (60 mL) and gradual addition of benzene (120 mL); m.p. 172–174°, $[\alpha]_D$ −98°, $[\alpha]_{578}$ −102°, $[\alpha]_{546}$ −115°, $[\alpha]_{436}$ −190°, $[\alpha]_{365}$ −286° (*c* 1.0, water; 5 min); $[\alpha]_D$ −84°, $[\alpha]_{578}$ −88°, $[\alpha]_{546}$ −100°, $[\alpha]_{436}$ −166°, $[\alpha]_{365}$ −250° (5 h, final value); ν_{max} 3600–2200 (OH, NH_2^+), 1640 (H_2O), and 1560 cm^{-1} (NH_2^+); ^{1}H-n.m.r. data (1:1 D_2O–CF_3CO_2H): δ 5.62 (d, H-1, $J_{1,2}$ 3.3 Hz, α anomer) and 5.17 (d, H-1, $J_{1,2}$ 8.3 Hz, β anomer).

Anal. Calc. for $C_8H_{18}ClNO_5 \cdot H_2O$: C, 36.72; H, 7.70; Cl, 13.55; N, 5.35. Found: C, 36.63; H, 7.42; Cl, 13.87; N, 5.27.

*1,3,4,6-Tetra-*O*-benzoyl-2-deoxy-2-(*N*-ethylbenzamido)-α-*L*-glucopyranose* (**10**). — To a solution of **9** (1 g, 3.8 mmol) in pyridine (10 mL) at 0° was added benzoyl chloride (3.6 mL, 31 mmol), and the mixture was kept for 24 h at 0° and poured into ice–water (300 mL) containing sodium hydrogencarbonate (10 g). The solid product (3.0 g, quantitative) was twice recrystallized from abs. ethanol; m.p. 218–220°, $[\alpha]_D$ −19°, $[\alpha]_{578}$ −20°, $[\alpha]_{546}$ −21°, $[\alpha]_{436}$ −18°, $[\alpha]_{365}$ +15° (*c* 0.7, chloroform); ν_{max} 1720, 1710 (C=O ester), 1620 (C=O amide), 1590, 1570, and 710 cm^{-1} (phenyl); ^{1}H-n.m.r. data ($CDCl_3$): δ 8.30–7.10 (m, 25 H, 5 Ph), 6.71 (d, 1 H, H-1, $J_{1,2}$ 3.3 Hz), 6.36 (dd, 1 H, H-3, $J_{2,3}$ 10.7, $J_{3,4}$ 9.3 Hz), 5.64 (m, 1 H, H-4, $J_{4,5}$ ~8 Hz), 5.07 (m, 1 H, H-2), 4.70–4.30 (m, 3 H, H-5,6,6'), 3.60 (m, 2 H, CH_2), and 0.89 (m, 3 H, CH_3).

Anal. Calc. for $C_{43}H_{37}NO_{10}$: C, 70.97; H, 5.12; N, 1.92. Found: C, 70.92; H, 5.25; N, 1.96.

*2-Deoxy-2-(propylamino)-α-*L*-glucopyranose hydrochloride* (**11**). — A solution of **6** (16.7 g, 64.8 mmol) in M hydrochloric acid (140 mL) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% palladium-on-barium sulfate (7 g), and the mixture was processed as described for the preparation of **9**, to give a solid product (11.6 g, 59%); m.p. 174–175°, $[\alpha]_D$ −93°, $[\alpha]_{578}$ −97°, $[\alpha]_{546}$ −109°, $[\alpha]_{436}$ −181°, $[\alpha]_{365}$ −271° (*c* 1.0, water; 5 min); $[\alpha]_D$ −79°, $[\alpha]_{578}$ −83°, $[\alpha]_{546}$ −94°, $[\alpha]_{436}$ −155.5°, $[\alpha]_{365}$ −233.5° (3 h, final value); ν_{max} 3600–2300 (OH, NH_2^+) and 1575 cm^{-1} (NH_2^+).

Anal. Calc. for $C_9H_{20}ClNO_5$: C, 41.94; H, 7.82; Cl, 13.75; N, 5.43. Found: C, 41.70; H, 8.10; Cl, 13.90; N, 5.50.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(*N*-propylacetamido)-α-*L*-glucopyranose* (**12**). — To a suspension of **11** (1 g, 3.9 mmol) in pyridine (2.5 mL) was added acetic anhydride (2.5 mL, 24.5 mmol), the mixture was processed as described for the preparation of **3**, and the organic layer was evaporated to a syrup; after addition of ether, compound **12** was obtained crystalline (0.7 g, 40%); m.p. 112–113°, $[\alpha]_D$ −115°, $[\alpha]_{578}$ −119°, $[\alpha]_{546}$ −134.5°, $[\alpha]_{436}$ −216°, $[\alpha]_{365}$ −312° (*c* 0.4, chloroform); ν_{max} 1740 (C=O, ester) and 1645 cm^{-1} (C=O, amide).

Anal. Calc. for $C_{19}H_{29}NO_{10}$: C, 52.90; H, 6.78; N, 3.25. Found: C, 53.25; H, 6.76; N, 3.20.

*1,3,4,6-Tetra-*O*-benzoyl-2-deoxy-2-(*N*-propylbenzamido)-α-*L*-glucopyranose* (**13**). — Benzoylation of **11** (0.5 g, 1.9 mmol) with benzoyl chloride–pyridine as described for **10** gave compound **13** (0.5 g, 65%). The crude product was recrystal-

lized from ethanol; m.p. 224–225°, $[\alpha]_{578}$ −35°, $[\alpha]_{546}$ −38°, $[\alpha]_{436}$ −47°, $[\alpha]_{365}$ −35° (*c* 0.4, chloroform); ν_{max} 1720 and 1710 (C=O, ester), 1620 (C=O, amide), 1590, 1575, and 710 cm^{-1} (phenyl); p.m.r. data ($CDCl_3$): δ 8.40–7.10 (m, 25 H, 5 Ph), 6.72 (d, 1 H, H-1, $J_{1,2}$ 3.2 Hz), 6.37 (dd, 1 H, H-3), $J_{2,3}$ 11.3, $J_{3,4}$ 9.3 Hz), 5.64 (m, 1 H, H-4), 5.05 (m, 1 H, H-2), 4.70–4.30 (m, 3 H, H-5,6,6'), 3.42 (m, 2 H, CH_2), 1.30 (m, 2 H, CH_2), and 0.50 (m, 3 H, CH_3).

Anal. Calc. for $C_{44}H_{44}NO_{10}$: C, 71.25; H, 5.26; N, 1.89. Found: C, 71.21; H, 5.40; N, 1.80.

2-Deoxy-2-(ethylamino)-L-mannose hydrochloride (**14**). — A solution of **8** (20.4 g, 0.1 mol) in M hydrochloric acid (270 mL) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% palladium-on-barium sulfate (15 g). The reaction mixture was processed as described for the preparation of **9**. After filtration of the ammonium chloride crystals, the filtrate was evaporated, and the residue was treated by repeatedly adding and evaporating abs. ethanol and benzene, to yield amorphous, very hygroscopic **14** (~23 g) that was used in the preparation of **21** and **23** without purification.

3-Ethyl-1-phenyl-(1,2-dideoxy-α-L-glucofurano)[2,1-d]imidazolidine-2-thione (**15**). — To a solution of **9** (4.0 g, 15.3 mmol) in water (10 mL) were added $NaHCO_3$ (1.4 g, 16.4 mmol), phenyl isothiocyanate (3.0 mL, 24.7 mmol), and 96% ethanol (35 mL). The mixture was heated, with stirring, for 4 h at 40°; acetic acid (5 mL) was added, and the solution was heated for 1 h. The solvent was evaporated under diminished pressure, and the residue was treated with water and ether to give a crystalline product (4.9 g, 93%). Recrystallized twice from water, it gave colorless needles; m.p. 165–167°, $[\alpha]_D$ −23°, $[\alpha]_{578}$ −23°, $[\alpha]_{546}$ −24°, $[\alpha]_{436}$ −21°, $[\alpha]_{365}$ +32° (*c* 0.5, pyridine); λ_{max}^{EtOH} 244 nm (ε_{mM} 17.40); ν_{max} 3600–3000 (OH), 1610 (H_2O), 765, and 695 cm^{-1} (phenyl).

Anal. Calc. for $C_{15}H_{20}N_2O_4S \cdot H_2O$: C, 52.62; H, 6.48; N, 8.18; S, 9.36. Found: C, 52.31; H, 6.44; N, 8.46; S, 9.78. Formic acid produced: 0.2 mol.

3-Ethyl-1-phenyl-(3,5,6-tri-O-acetyl-1,2-dideoxy-α-L-glucofurano)[2,1-d]-imidazolidine-2-thione (**16**). — Conventional treatment of **15** (1.0 g, 2.9 mmol) with pyridine (5 mL) and acetic anhydride (5 mL) gave **16** (1.32 g, quant.). Crystallized from 96% ethanol, it had m.p. 128–130°, $[\alpha]_D$ −51.5°, $[\alpha]_{578}$ −54°, $[\alpha]_{546}$ −61°, $[\alpha]_{436}$ −91°, $[\alpha]_{365}$ −102° (*c* 0.7, chloroform); ν_{max} 1740 (C=O), 1580, 750, and 695 cm^{-1} (phenyl); p.m.r. data are given in Table I.

Anal. Calc. for $C_{21}H_{26}N_2O_7S$: C, 55.99; H, 5.82; N, 6.22; S, 7.12. Found: C, 56.13; H, 5.82; N, 6.36; S, 7.20.

1-(4-Bromophenyl)-3-ethyl-(1,2-dideoxy-α-L-glucofurano)[2,1-d]imidazolidine-2-thione (**17**). — To a solution of **9** (4.0 g, 15.3 mmol) in water (10 mL) were added $NaHCO_3$ (1.38 g, 16.4 mmol), 4-bromophenyl isothiocyanate (5.27 g, 24.6 mmol), and 96% ethanol (35 mL). The mixture was processed as described for the preparation of **15**, to give a crystalline product (6.0 g, 91%) which was purified by two recrystallizations from 50% ethanol; needles, m.p. 110–111°, $[\alpha]_D$ −37°, $[\alpha]_{578}$

$-38°$, $[\alpha]_{546}$ $-43°$, $[\alpha]_{436}$ $-61.5°$, $[\alpha]_{365}$ $-56°$ (*c* 0.5, pyridine); λ_{max}^{EtOH} 244 nm (ε_{mM} 20.9); ν_{max} 3600–3100 (OH), 1630 (H_2O), and 830 cm^{-1} (aryl, *p*-subst.).

Anal. Calc. for $C_{15}H_{19}BrN_2O_4S \cdot H_2O$: C, 42.76; H, 5.02; Br, 18.97; N, 6.65; S, 7.61. Found: C, 42.74; H, 5.04; Br, 19.31; N, 6.57; S, 7.98. Formic acid produced: 0.2 mol.

*1-(4-Bromophenyl)-3-ethyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-*L*-glucofurano)-[2,1-*d*]imidazolidine-2-thione* (**18**). — Conventional treatment of **17** (1.0 g, 2.5 mmol) with pyridine (3 mL) and acetic anhydride (4 mL) gave **18** (1.3 g, 96%). Crystallized from 96% ethanol, it had m.p. 129–130°, $[\alpha]_D$ $-52°$, $[\alpha]_{578}$ $-55°$, $[\alpha]_{546}$ $-62°$, $[\alpha]_{436}$ $-97.5°$, $[\alpha]_{365}$ $-124°$ (*c* 1.0, chloroform); ν_{max} 1730 (C=O) and 830 cm^{-1} (aryl, *p*-subst.); p.m.r. data are given in Table I.

Anal. Calc. for $C_{21}H_{25}BrN_2O_7S$: C, 47.64; H, 4.76; Br, 15.09; N, 5.29; S, 6.06. Found: C, 47.78; H, 4.73; Br, 14.79; N, 5.32; S, 6.46.

*1-Phenyl-3-propyl-(1,2-dideoxy-α-*L*-glucofurano)[2,1-*d*]imidazolidine-2-thione* (**19**). — To a solution of **11** (3.0 g, 11.6 mmol) in water (7.5 mL) were added $NaHCO_3$ (0.97 g, 11.6 mmol), phenyl isothiocyanate (1.4 mL, 11.6 mmol), and 96% ethanol (30 mL). The reaction mixture was processed as described for the preparation of **15**, to give a crystalline product (0.9 g, 22%). Recrystallized from ethanol, it had m.p. 124–125°, $[\alpha]_D$ $-18°$, $[\alpha]_{578}$ $-19°$, $[\alpha]_{546}$ $-21°$, $[\alpha]_{436}$ $-19°$, $[\alpha]_{365}$ $+24°$ (*c* 0.25, pyridine); λ_{max}^{EtOH} 251 nm (ε_{mM} 8.2); ν_{max} 3500–3100 (OH), 1595, 760, and 700 cm^{-1} (phenyl).

Anal. Calc for $C_{16}H_{22}N_2O_4S$: C, 56.79; H, 6.55; N, 8.28; S, 9.47. Found: C, 56.68; H, 6.92; N, 8.08; S, 9.63. Formic acid produced: 0.2 mol.

*1-Phenyl-3-propyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-*L*-glucofurano)[2,1-*d*]-imidazolidine-2-thione* (**20**). — To a solution of **19** (0.1 g, 0.3 mmol) in pyridine (1 mL) was added acetic anhydride (1 mL). After being kept for 24 h at room temperature, the mixture was poured into ice–water, and extracted with chloroform (3 × 15 mL); the extracts were combined, successively washed with saturated $CuSO_4$ solution and water, dried (Na_2SO_4), and evaporated. The resulting syrup crystallized from carbon tetrachloride (yield 0.08 g, 61%); m.p. 80–81°, $[\alpha]_D$ $-38°$, $[\alpha]_{578}$ $-38.5°$, $[\alpha]_{546}$ $-43°$, $[\alpha]_{436}$ $-62.5°$, $[\alpha]_{365}$ $-64°$ (*c* 0.4, chloroform); ν_{max} 1745 and 1730 (C=O), 1590, 760, and 695 cm^{-1} (phenyl); p.m.r. data are given in Table I.

Anal. Calc. for $C_{22}H_{28}N_2O_7S \cdot CCl_4$: C, 44.67; H, 4.56; N, 4.53; S, 5.18. Found: C, 44.95; H, 4.90; N, 4.59; S, 4.60.

*3-Ethyl-1-phenyl-(1,2-dideoxy-β-*L*-mannofurano)[2,1-*d*]imidazolidine-2-thione* (**21**). — To a solution of **14** (4.1 g, 16.8 mmol) in water (13 mL) were added $NaHCO_3$ (1.42 g, 16.9 mmol), phenyl isothiocyanate (3.0 mL, 24.9 mmol), and 96% ethanol (36 mL). The reaction mixture was processed as described for the preparation of **15**, to give a crystalline product (1.73 g, 32%) which was purified by several recrystallizations from 96% ethanol; plates, m.p. 186–188°, $[\alpha]_D$ $+131°$, $[\alpha]_{578}$ $+137°$, $[\alpha]_{546}$ $+157°$, $[\alpha]_{436}$ $+283°$, $[\alpha]_{365}$ $+475°$ (*c* 0.5, pyridine); λ_{max}^{EtOH} 246 nm (ε_{mM} 16.7); ν_{max} 3600–3000 (OH), 1590, 770, and 700 cm^{-1} (phenyl).

Anal. Calc. for $C_{15}H_{20}N_2O_4S$: C, 55.54; H, 6.21; N, 8.64; S, 9.88. Found: C, 55.47; H, 6.11; N, 8.54; S, 10.03. Formic acid produced: 0.2 mol.

3-Ethyl-1-phenyl-(3,5,6-tri-O-acetyl-1,2-dideoxy-β-L-mannofurano)[2,1-d]-imidazolidine-2-thione (**22**). — Conventional treatment of **21** (0.75 g, 2.3 mmol) with pyridine (3 mL) and acetic anhydride (3.8 mL) gave **22** (0.98 g, 99%). Crystallized from 65% ethanol, it had m.p. 158–160°, $[\alpha]_D$ +113°, $[\alpha]_{578}$ +117°, $[\alpha]_{546}$ +134°, $[\alpha]_{436}$ +238°, $[\alpha]_{365}$ +394° (*c* 1.0, chloroform); ν_{max} 1730 (C=O), 1585, 770, and 700 cm^{-1} (phenyl); p.m.r. data are given in Table I.

Anal. Calc. for $C_{21}H_{26}N_2O_7S$: C, 55.99; H, 5.82; N, 6.22; S, 7.12. Found: C, 55.95; H, 5.83; N, 6.22; S, 7.36.

1-(4-Bromophenyl)-3-ethyl-(1,2-dideoxy-β-L-mannofurano)[2,1-d]imidazolidine-2-thione (**23**). — To a solution of **14** (4.1 g, 16.8 mmol) in water (13 mL) were added $NaHCO_3$ (1.42 g, 16.9 mmol), 4-bromophenyl isothiocyanate (5.4 g, 25.1 mmol), and 96% ethanol (36 mL). The mixture was heated, with stirring, for 2 h at 40–45°, acetic acid (6 mL) was added, and the solution was heated for a further 1 h. During the reaction, a crystalline precipitate separated, and this was filtered off, washed with water, and dried (0.4 g); this product was identified as 1,3-bis(4-bromophenyl)thiourea. The filtrate was evaporated under diminished pressure, and the thick syrup resulting was treated with water (50 mL), made neutral with $NaHCO_3$, and washed with ether (3 × 20 mL). A water-insoluble, yellow oil separated from the aqueous phase, which was then decanted; treatment of the oil with ethanol (10 mL) gave a crystalline product (1.79 g, 27%); recrystallized from 96% ethanol, it gave colorless needles; m.p. 150–152°, $[\alpha]_D$ +140°, $[\alpha]_{578}$ +147°, $[\alpha]_{546}$ +168.5°, $[\alpha]_{436}$ +308°, $[\alpha]_{365}$ +526° (*c* 1.0,pyridine); λ_{max}^{EtOH} 246 nm (ε_{mM} 19.9); ν_{max} 3600–3000 (OH), 1580, and 825 cm^{-1} (aryl, *p*-subst.).

Anal. Calc. for $C_{15}H_{19}BrN_2O_4S$: C, 44.67; H, 4.75; Br, 19.81; N, 6.95; S, 7.95. Found: C, 44.66; H, 4.87; Br, 19.64; N, 7.13; S, 8.15. Formic acid produced: 0.2 mol.

1-(4-Bromophenyl)-3-ethyl-(3,5,6-tri-O-acetyl-1,2-dideoxy-β-L-mannofurano)[2,1-d]imidazolidine-2-thione (**24**). — Conventional treatment of **23** (0.81 g, 2.0 mmol) with pyridine (2 mL) and acetic anhydride (3.3 mL) gave **24** (1.0 g, 94%). Crystallized from 96% ethanol, it had m.p. 167–169°, $[\alpha]_D$ +120°, $[\alpha]_{578}$ +125°, $[\alpha]_{546}$ +143°, $[\alpha]_{436}$ +257°, $[\alpha]_{365}$ +432° (*c* 1.0, chloroform); ν_{max} 1730 (C=O), 1575, and 830 cm^{-1} (aryl, *p*-subst.); p.m.r. data are given in Table I.

Anal. Calc. for $C_{21}H_{25}BrN_2O_7S$: C, 47.64; H, 4.76; Br, 15.09; N, 5.29; S, 6.06. Found: C, 47.78; H, 4.77; Br, 15.43; N, 5.13; S, 5.86.

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