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Note

One-step synthesis of non-anomeric sugar isothiocyanates from sugar azides

M. Isabel García-Moreno,[a] Paula Díaz-Pérez,[a] Juan M. Benito,[a] Carmen Ortiz Mellet,[a,*] Jacques Defaye,[b] José M. García Fernández[c,*]

[a]*Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, Aptdo. 553, E-41071 Sevilla, Spain*
[b]*CNRS and Université Joseph Fourier-Grenoble I (UMR 5063), Département de Pharmacochimie Moléculaire-Glucides, BP 138, F-38243 Meylan, France*
[c]*Instituto de Investigaciones Químicas, CSIC, Américo Vespucio s/n, Isla de la Cartuja, E-41092 Sevilla, Spain*

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Dedicated to Professor Derek Horton on the occasion of his 70th birthday

Abstract

Tandem Staudinger–aza-Wittig reaction of primary azidodeoxy sugars with triphenylphosphine–carbon disulfide affords the corresponding primary deoxyisothiocyanato sugars in high yield. No products arising from O → N acyl migration or formation of dimeric carbodiimides were observed. Interestingly, a polymer-supported triarylphosphine can advantageously replace triphenylphosphine, thus limiting the purification step to a simple filtration process. The reaction also allows the preparation of 5-deoxy-5-isothiocyanato sugars, a hitherto unknown class of compounds, from the corresponding azide precursors. Secondary sugar azides bearing the azido group at an endocyclic carbon atom afforded much lower isothiocyanation yields under these reaction conditions.

Keywords: Sugar isothiocyanates; Sugar carbodiimides; Sugar iminophosphoranes; Aza-Wittig reaction; Staudinger reaction

Sugar isothiocyanates rank among the most versatile synthetic intermediates in carbohydrate chemistry. They play a key role in the preparation of a variety of functional groups as well as in the construction of heterocyclic ring systems allowing, simultaneously, the covalent attachment of a quite unrestricted variety of structures to the saccharide part.[1–3] This reactivity has been widely exploited in the case of glycosyl isothiocyanates, for which several practical syntheses have been developed.[4–9] In contrast, reports on the synthesis and reactions of carbohydrate derivatives bearing non-anomeric isothiocyanate functionalities are much more scarce. Except for some preparations of unsaturated sugar isothiocyanates by 3,3-sigmatropic rearrangement of allylic thiocyanates,[10–12] deoxyisothiocyanato sugars have been generally obtained by isothiocyanation of the corresponding amino sugars.[1] This approach presents some limitations in the case of O-acylated derivatives due to the possibility of simultaneous O → N acyl migration. Protection of the amino group as an enamine prior to O-acylation has been shown to prevent this side reaction to some extent.[13] Nevertheless, this sequence implies two additional protection/deprotection steps, with the subsequent decrease in the overall yield. The presence of acid-sensitive protecting groups, such as silyl ethers, is also problematic when thiophosgene, the most widely used isothiocyanation reagent, is employed.[14]

Since the amino group is often introduced via an azide precursor, the Staudinger reaction of the azido group with phosphine[15,16] and subsequent aza-Wittig type condensation[16,17] of the resulting iminophosphorane (λ^5-phosphazene, phosphine imine) with carbon disulfide is an attractive alternative for the preparation

* Corresponding authors. Fax: +34 954624960 (C.O.M.); Fax: +34 954460565 (J.M.G.F.)
E-mail addresses: mellet@us.es (C. Ortiz Mellet), jogarcia@cica.es (J.M. García Fernández).

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of sugar isothiocyanates. In the frame of a project directed towards the utilization of sugar thioureas,[18–20] carbodiimides[21–23] and azaheterocycles[24–26] in supramolecular chemistry and glycomimetic design, we have now examined the one-step preparation of deoxy-

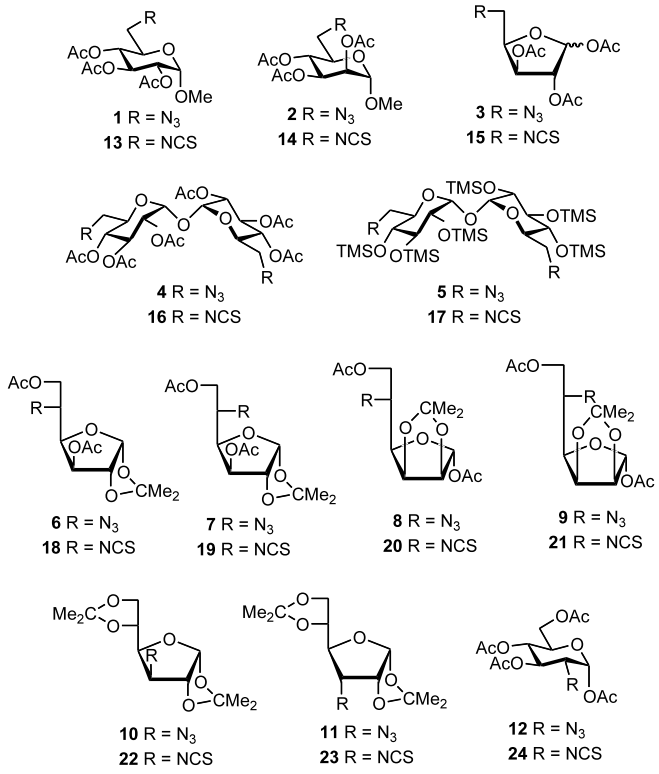
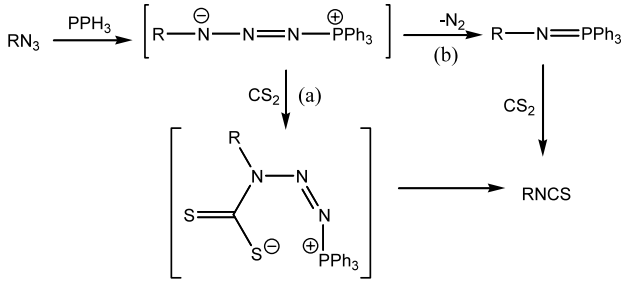


Fig. 1. Structures of azidodeoxy sugars **1**–**12** and deoxyisothiocyanato sugars **13**–**24**.

Table 1
Products formed by the action of triphenylphosphine or polymer-supported triphenylphosphine (1.1 equiv)[a] and carbon disulfide on azidodeoxy sugars

Substrate	Reaction conditions[b]	Product (%)[c]
1	A (PPh_3/polymeric PPh_3)	**13** (91/95)
2	A (PPh_3/polymeric PPh_3)	**14** (88/92)
3	A (PPh_3/polymeric PPh_3)	**15** (95/97)
4	A (PPh_3/polymeric PPh_3)	**16** (76/82)
5	A (PPh_3/polymeric PPh_3)	**17** (79/86)
6	B (PPh_3/polymeric PPh_3)	**18** (30/33)
7	B (PPh_3/polymeric PPh_3)	**19** (35/35)
8	B (PPh_3/polymeric PPh_3)	**20** (68/73)
9	B (PPh_3/polymeric PPh_3)	**21** (70/75)
10	B (PPh_3/polymeric PPh_3)	**22** (21/20)
11	C (PPh_3/polymeric PPh_3)	**23** (24/22)
12	C (PPh_3/polymeric PPh_3)	**24** (15/18)

[a] The mol/equiv ratio for substrates refers to azido groups.
[b] A: 10 equiv CS_2, room temperature, 16 h; B: 15 equiv CS_2, 40 °C, 48 h; C: 25 equiv CS_2, 80 °C, 48 h.
[c] Isolated yields.



Scheme 1. Mechanism of isothiocyanate formation from azide via transient phosphazide (a) and iminophosphorane intermediates (b).

isothiocyanato sugars by this procedure. Although the strategy has been reported[27] to fail in the case of glycosyl azides due to concomitant reaction between the incipient isothiocyanate and the remaining iminophosphorane, resulting in the corresponding symmetric carbodiimide, the lower reactivity of the non-anomeric isothiocyanate functionality towards nucleophiles was expected to allow a better control of the reaction. Homogeneous and heterogeneous conditions using triphenylphosphine and a polymer-supported triarylphosphine, respectively, have been considered. Mono- and disaccharide templates **1**–**12** (Fig. 1), including pyranose and furanose derivatives, bearing azido groups at primary and secondary positions and a variety of O-protecting groups have been chosen to illustrate the scope and limitations of the method. Reaction conditions and results are collected in Table 1.

Preliminary attempts to transform the primary azidodeoxy sugars **1**–**3** into the corresponding isothiocyanates in a stepwise manner by: (i) reaction with triphenylphosphine until disappearance of the starting azide (TLC) and; (ii) further addition of carbon disulfide led to significant proportions of 6-acetamido-6-deoxy derivatives in the reaction mixtures, arising from hydrolysis of the corresponding phosphinimine and subsequent acetyl migration. Actually, hydrolysis of iminophosphorane intermediates is a well-known method for the preparation of amino sugars from azide precursors.[28,29] Nevertheless, when the Staudinger reaction was conducted in the presence of a 10-fold excess of carbon disulfide in dioxane at room temperature, clean transformations into the target primary isothiocyanates **13**–**15** were achieved. A small excess of triphenylphosphine is necessary to warrant total consumption of the starting azide, thus facilitating chromatographic purification, since the reagent and the product have very similar retention factors (R_f) on silica gel using various eluent mixtures. No traces of the acetamido by-products or of the symmetric carbodiimides were observed. Probably, the reaction proceeds in this case through a transient phosphazide, a known

precursor of the iminophosphorane that undergoes direct addition to the heterocumulene reagent (Scheme 1, pathway a), thus minimizing side reactions. A similar mechanism has been previously proposed for the tandem Staudinger–aza-Wittig reaction of sugar azides with isothiocyanates.[22]

Our next interest was the direct transformation of the per-*O*-acetyl and per-*O*-trimethylsilyl 6,6′-diazido-6,6′-dideoxy-α,α′-trehalose derivatives **4** and **5** into the corresponding per-O-protected trehalose diisothiocyanates **16** and **17**, two key building blocks in the preparation of trehalose-based macrocyclic receptors.[30] Former syntheses from the diamine precursors were troublesome due to acyl migration and silyl ether lability. Under the above conditions, 76 and 79% isolated yields of **16** and **17**, respectively, were obtained after 16 h.

The preparation of 5-deoxy-5-isothiocyanatoaldohexofuranose derivatives, a hitherto unknown family of sugar isothiocyanates bearing an acetyl group at O-6 is particularly challenging. Attempts to synthesize these compounds from the corresponding amines resulted in the almost exclusive formation of the product of O-6 → N-5 acetyl migration, whereas in the absence of an O-protecting group the corresponding 5,6-(cyclic thiocarbamate) was the only reaction product. Although the 5-azido-5-deoxy sugars **6**–**9** showed a lower reactivity against the triphenylphosphine–carbon disulfide system as compared with primary azido sugars, the target isothiocyanates **18**–**21** could be obtained by using a 15-fold excess of carbon disulfide in dioxane at 40 °C. The reaction yield was, however, highly dependent on the monosaccharide template, ranging from 30–35% for the D-*gluco* and L-*ido* derivatives to 65–70% for the D-*manno* and L-*gulo* epimers.

Compounds **10**–**12**, bearing an azido group at a secondary endocyclic carbon atom, exhibited a much lower reactivity under the above tandem Staudinger–aza-Wittig isothiocyanation conditions. Formation of the isothiocyanate was not detected after 24 h at 40 °C. Using a 25-fold excess of carbon disulfide and heating at 80 °C for 48 h afforded complex mixtures from which the isothiocyanates **22**–**24** were isolated in low yield. Probably, the steric constrain imposed by the sugar ring hinders both the coupling of the azide with the phosphine and the subsequent condensation of the phophazide adduct with carbon disulfide. Most likely, extrusion of molecular nitrogen to give the iminophosphorane derivative is now faster (Scheme 1, pathway b). The ability of this synthetic intermediate to react with both the remaining azide and the incipient isothiocyanate, as well as its tendency to undergo hydrolysis to the corresponding amine, results in the formation of several by-products that complicate the purification step.

The need for a chromatographic separation of triphenylphosphine sulfide, which is formed in the reaction, and excess triphenylphosphine represents a shortcoming, and actually a limitation of the method itself, especially considering its utilisation in small-scale reactions. For this reason, replacement of triphenylphosphine by a polymer-supported triarylphosphine, the commercially available polystyryl diphenylphosphine resin, was considered. This resin has already been used successfully in Staudinger and aza-Wittig transformations of azides in nucleoside series.[31,32] In our case, the reaction of azides with the polymer-supported phosphine–carbon disulfide system afforded almost identical results as those discussed above that used homogeneous reaction conditions. The most important feature of the heterogeneous protocol is that now removal of the polymer-supported triarylphosphine and triarylphosphine sulfide requires only filtration of the polymeric material. In the case of the primary azidodeoxy sugars **1**–**5**, evaporation of the filtrate led to the corresponding isothiocyanates **13**–**17** in pure form without need of any chromatographic separation. For the secondary azidodeoxy sugars **6**–**12**, the presence of additional by-products in the reaction mixtures diminished, and in most cases actually counterbalanced, the advantage of using the polystyryl diphenylphosphine resin in comparison with triphenylphosphine.

In conclusion, we have shown that direct isothiocyanation of per-O-protected primary azidodeoxy sugars with triphenylphosphine–carbon disulfide is a convenient synthetic methodology for the mild and high yielding preparation of the corresponding non-anomeric sugar isothiocyanates. The method is compatible with the presence of acyl as well as acid-sensitive silyl ether groups. Since the primary hydroxyl group of monosaccharides can be converted directly into the corresponding azide,[33] this route provides access to the per-O-protected deoxyisothiocyanates in three steps from the commercial sugar. Moreover, triphenylphosphine can be advantageously replaced by a polymer-supported triarylphosphine, which avoids any chromatographic purification. The reactivity of secondary azidodeoxy sugars under the same conditions is considerably lowered and depends essentially upon the configuration of the sugar template. The method still compares favourably with isothiocyanation of amino sugars for exocyclic secondary positions, allowing the preparation of the new 6-*O*-acetyl-5-deoxy-5-isothiocyanato aldohexofuranoses **18**–**21**. In the case of monosaccharides bearing an azido group at an endocyclic carbon atom, however, isothiocyanation of the corresponding amino sugar is still the method of choice.

1. Experimental

Materials and methods.—A Perkin–Elmer model 141 MC polarimeter and 1 dm cells were used for measure-

ments of specific rotations. IR spectra were recorded on a Bomem Michelson MB-120 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 500 (125.7) and 300 (75.5) MHz with, respectively, Bruker 500 DRX spectrometers and 300 AMX spectrometers. Chemical shifts are given in ppm with reference to Me_4Si as the internal standard. FAB mass spectra were obtained with a Kratos MS-80 RFA instrument using the following operating conditions: the primary beam consisted of Xe atoms with a maximum energy of 8 keV; the samples were dissolved in *m*-nitrobenzylalcohol, and the positive ions were separated and accelerated over a potential of 7 keV; NaI was added as cationizing agent. TLC was performed with E. Merck precoated TLC plates, Silica Gel $30F_{254}$, with visualisation by UV light and by charring with 10% H_2SO_4. Column chromatography was carried out with Silica Gel 60 (E. Merck, 230–400 mesh). Microanalyses were performed by the Instituto de Investigaciones Químicas (CSIC, Seville).

Methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (**1**) and methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-mannopyranoside[34] (**2**) were prepared from commercial-grade methyl glycopyranosides by direct replacement of the primary OH-6 by azide with the triphenylphosphine–CBr_4–NaN_3 system[33] and further acetylation. 1,2,3-Tri-*O*-acetyl-5-azido-5-deoxy-D-xylofuranose (**3**) was prepared from 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose[35] by deacetalation with aq TFA and subsequent conventional acetylation. 2,3,4,2′,3′,4′-Hexa-*O*-acetyl-6,6′-diazido-6,6′-dideoxy-α,α′-trehalose (**4**) and the hexa-*O*-trimethylsilylated derivative **5** were obtained from the 6,6′-diazido-6,6′-dideoxy precursor[36] by conventional acetylation and silylation (TMSCl–hexamethyldisilazane), respectively. Conventional acetylation of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*- (or β-L-*ido*-) furanoses[37] afforded the 3,6-diacetates **6** and **7**. Similarly, acetylation of reducing 5-azido-5-deoxy-2,3-*O*-isopropylidene-α-D-*manno*- (or L-*gulo*-) furanose precursors[38,39] led to the corresponding 1,6-diacetates **8** and **9** with an α-anomeric configuration. 3-Azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**10**) and the corresponding α-D-*allo* derivative (**11**) were obtained in two steps from commercial 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose as reported.[28] 1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranose (**12**) was prepared by the triflyl azide reaction of 2-amino-2-deoxy-D-glucose, following the procedure reported by Alper et al.,[40] and subsequent acetylation. Polymer-supported triphenylphosphine was purchased from Aldrich.

Typical procedure for the preparation of deoxyisothiocyanato sugars under homogeneous reaction conditions.—To a solution of the corresponding azidodeoxy sugar (0.1–0.3 mmol) and CS_2 (10 to 25 equiv/mol) in anhyd dioxane (5 mL) was added triphenylphosphine (1.1 equiv/mol). The reaction mixture was stirred at 20–80 °C for 16–48 h under Ar, then concd, and the residue was purified by silica gel column chromatography using mixtures of EtOAc–petroleum ether as eluents. Experimental conditions and yields have been summarised in Table 1.

Typical procedure for the preparation of deoxyisothiocyanato sugars under heterogeneous reaction conditions.—To a solution of the corresponding azidodeoxy sugar (0.1 mmol) and CS_2 (10 to 25 equiv/mol) in anhyd dioxane (5 mL) was added polymer-supported triphenylphosphine (40 mg, loaded with ca. 3 mmol PPh_3/g). The reaction mixture was shaken under Ar at the temperaure previously used for the homogeneous reaction conditions (Table 1). The suspension was filtered, and the resin was washed with dioxane (6 × 5 mL). In the case of **1**–**5**, evaporation of the solution afforded the pure isothiocyanates **13**–**17**. In the case of the secondary azido sugar precursors **6**–**12**, the reaction mixtures contained several by-products in addition to the target isothiocyanate. Column chromatography then afforded pure **18**–**24** in similar yield to that obtained under homogeneous reaction conditions.

The known deoxyisothiocyanato sugars **13**,[34] **14**,[34] **15**,[24] **16**,[36] **17**,[1,30] **22**,[28] **23**,[28] and **24**[41] showed physical and spectroscopic data identical to literature examples. Their identity was further confirmed by comparison with authentic samples.

3,6-Di-O-*acetyl-5-deoxy-1,2*-O-*isopropylidene-5-isothiocyanato-α-D-glucofuranose* (**18**).—Isolated as an amorphous solid after column chromatography (1:4 EtOAc–petroleum ether); $[\alpha]_D$ −24.1° (*c* 1.0, CH_2Cl_2); IR (KBr) 2988, 2093, 1750, 1645, 1379, 1221, and 1092 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.30 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-3), 4.52 (d, 1 H, H-2), 4.51 (dd, 1 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.34 (dd, 1 H, $J_{3,4}$ 3.1, $J_{4,5}$ 9.1 Hz, H-4), 4.20 (dd, 1 H, $J_{5,6b}$ 6.4 Hz, H-6b), 4.14 (m, 1 H, H-5), 2.14, 2.12 (2 s, each 3 H, 2 MeCO), 1.52, 1.31 (2 s, each 3 H, CMe_2); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.3, 169.3 (CO), 138.6 (NCS), 112.7 (*C*Me_2), 105.1 (C-1), 82.9 (C-2), 77.0 (C-4), 77.7 (C-3), 63.6 (C-6), 54.8 (C-5), 26.7, 26.1 (C*Me*$_2$), 20.7, 20.6 (*Me*CO); FABMS: *m*/*z* 346 (20%, $[M+H]^+$). Anal. Calcd for $C_{14}H_{19}NO_7S$: C, 48.69; H, 5.55; N, 4.06. Found: C, 48.55; H, 5.54; N, 4.00.

3,6-Di-O-*acetyl-1,2*-O-*isopropylidene-5-deoxy-5-isothiocyanato-β-L-idofuranose* (**19**).—Isolated as an amorphous solid after column chromatography (1:4 EtOAc–petroleum ether); $[\alpha]_D$ −8.1° (*c* 1.0, CH_2Cl_2); IR (KBr) 2991, 2080, 1746, 1381, and 1111 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.25 (d, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.56 (d, 1 H, H-2), 4.30 (dd, 1 H, $J_{4,5}$ 4.7 Hz, H-4), 4.24 (dd, 1 H, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.23 (dd, 1 H, $J_{5,6b}$ 1.0 Hz, H-6b), 4.16 (td, 1 H, H-5), 2.16, 2.10 (2 s, each 3 H, 2 MeCO), 1.53, 1.32 (2 s, each 3 H, CMe_2); ^{13}C NMR (125.7

MHz, $CDCl_3$): δ 170.2, 169.8 (CO), 137.5 (NCS), 112.5 (CMe_2), 104.5 (C-1), 83.3 (C-2), 76.9 (C-3), 76.1 (C-4), 63.5 (C-6), 55.5 (C-5), 26.7, 26.1 (CMe_2), 20.7, 20.5 (*Me*CO); FABMS: m/z 368 (100% $[M+Na]^+$). Anal. Calcd for $C_{14}H_{19}O_7NS$: C, 48.69; H, 5.54; N, 4.05. Found: C, 48.23; H, 5.23; N, 3.89.

1,6-Di-O-*acetyl-5-deoxy-2,3*-O-*isopropylidene-5-isothiocyanato-α*-D-*mannofuranose* (**20**).—Isolated as an amorphous solid after column chromatography (1:3 EtOAc–petroleum ether); $[\alpha]_D$ +16.9° (*c* 1.0, CH_2Cl_2); IR (KBr) 2928, 2054, 1752, 1651, 1386, 1236, and 1093 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.12 (s, 1 H, H-1), 4.88 (d, 1 H, $J_{3,4}$ 3.4, $J_{2,3}$ 5.8 Hz, H-3), 4.70 (d, 1 H, H-2), 4.47 (q, 1 H, $J_{4,5}=J_{5,6a}=J_{5,6b}$ 9.1 Hz, H-5), 4.26 (m, 2 H, H-6a, H-6b), 4.14 (dd, 1 H, H-4), 2.22, 2.07 (2 s, each 3 H, 2 MeCO), 1.48, 1.35 (2 s, each 3 H, CMe_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.2, 168.9 (CO), 137.9 (NCS), 113.5 (CMe_2), 100.5 (C-1), 84.5 (C-2), 79.9 (C-4), 77.3 (C-3), 63.4 (C-6), 54.8 (C-5), 25.9, 24.6 (CMe_2), 20.8, 20.6 (*Me*CO); FABMS: m/z 386 (50%, $[M+Na]^+$). Anal. Calcd for $C_{14}H_{19}NO_7S$: C, 48.69; H, 5.55; N, 4.06. Found: C, 48.51; H, 5.46; N, 3.92.

1,6-Di-O-*acetyl-5-deoxy-5-isothiocyanato-2,3*-O-*isopropylidene-β*-L-*gulofuranose* (**21**).—Isolated as an amorphous solid after column chromatography (1:3 EtOAc–petroleum ether); $[\alpha]_D$ +79.4° (*c* 1.0, CH_2Cl_2); IR (KBr) 2994, 2058, 1744, 1651, 1393, 1225, and 1094 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.17 (s, 1 H, H-1), 4.74 (dd, 1 H, $J_{3,4}$ 3.4, $J_{2,3}$ 5.8 Hz, H-3), 4.70 (d, 1 H, H-2), 4.35 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.32 (dd, 1 H, $J_{5,6b}$ 3.6 Hz, H-6b), 4.26 (ddd, 1 H, $J_{4,5}$ 8.4 Hz, H-5), 4.16 (dd, 1 H, H-4), 2.12, 2.08 (2 s, each 3 H, 2 MeCO), 1.46, 1.29 (2 s, each 3 H, CMe_2; $^{13}CNMR$ (125.7 MHz, $CDCl_3$): δ 170.3, 169.0 (CO), 137.3 (NCS), 113.8 (CMe_2), 100.2 (C-1), 85.4 (C-2), 81.0 (C-4), 78.6 (C-3), 62.9 (C-6), 56.5 (C-5), 25.9, 24.7 (CMe_2), 20.9, 20.7 (*Me*CO); FABMS: m/z 386 (50%, $[M+Na]^+$). Anal. Calcd for $C_{14}H_{19}NO_7S$: C, 48.69; H, 5.55; N, 4.06. Found: C, 48.66; H, 5.34; N, 3.97.

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