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Ring contraction of glycopyranosyl enamines: an easy route to furanoid thioglycosides of 5-aminosugars

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Received 23 April 2004; accepted 24 May 2004
Available online 19 June 2004

Abstract—The reaction of glycohexapyranosyl enamines, having 2- and 3-hydroxyl groups in a *cis*-relationship with 2,2-dimethoxypropane, induces ring contraction of the sugar ring with formation of 2,3-*O*-isopropylidene furanoid glycosylenamines. 5-*O*-Mesylation of these compounds, followed by formation of anhydroazasugars and nucleophilic ring opening, with thiols, produces alkyl and aryl thiofuranosides of 5-aminosugars.
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1. Introduction

Glycosylenamines can be easily and stereoselectively transformed into anhydroazasugars;[1] and, in this way, they are versatile starting materials for preparing five-,[2] six-,[3] and seven[4]-membered polyhydroxyiminocyclitols with enzyme inhibitory activity.[5]

Dialkoxycarbonyl vinyl groups have also been used as temporary *N*-protecting groups of aminosugars and glycosylamines, in the preparation of isothiocyanatosugars, thioureidosugars, and other derivatives[6] useful in glycoconjugate synthesis. We have found no data on anomeric equilibria or ring contraction of glycopyranosyl enamines.

At the same time, thioglycosides, a type of glycoside in which the anomeric oxygen atom has been substituted by a sulfur atom, have been widely used as efficient glycosyl donors in glycosylation reactions for the syntheses of complex carbohydrates.[7] Over the last few years, several new syntheses of aryl and alkyl thioglycopyranosides and their use in programmable[8] and non-programmable[9] preparations of pyranoid oligosaccharides have been reported. Oligosaccharide-containing furanose moieties are important constituents in the cell walls of lower organisms such as bacteria,[10] fungi,[11] and plants,[12] and are crucial for the survival of these organisms. Consequently, there has been increasing interest in the syntheses of furanose oligosaccharides, although the bibliographic data are more scarce than in the case of the pyranose counterparts. Several alkyl and aryl 1-thiofuranosides,[13] useful as glycofuranosyl donors in the preparation of di- and oligofuranosides, have recently been described.[14] The thioglycosides have also been used to prepare poly-*O*-protected 1-hydroxysugars, as the thioalkyl and thiophenyl groups can be selectively removed from poly-*O*-protected sugars with different *O*-protecting groups.[15] From a pharmaceutical point of view, the thioglycosides are useful as antithrombotic agents.[16] Recently, we have reported the preparation of monocyclic[17] and bicyclic[17,18] azasugar thioglycosides, in which the oxygen atom of the sugar ring is substituted by a nitrogen atom. The method is based on the nucleophilic opening of intermediate anhydroazasugar derivatives. As far as we are aware, there are no data on furanoid thioglycosides having an amino group on the sugar chain, while in the case of pyranoid analogues the amino group is found only on the two position[8] (D-*gluco* and D-*galacto* configurations).

Herein we report the synthesis of the first alkyl **6** and **12**–**14** and aryl **15** 1-thioglycosides of furanoid 5-aminosugars starting from glycosyl enamines **1** and **7**. This method involves a ring contraction reaction of the starting enaminosugar derivative.

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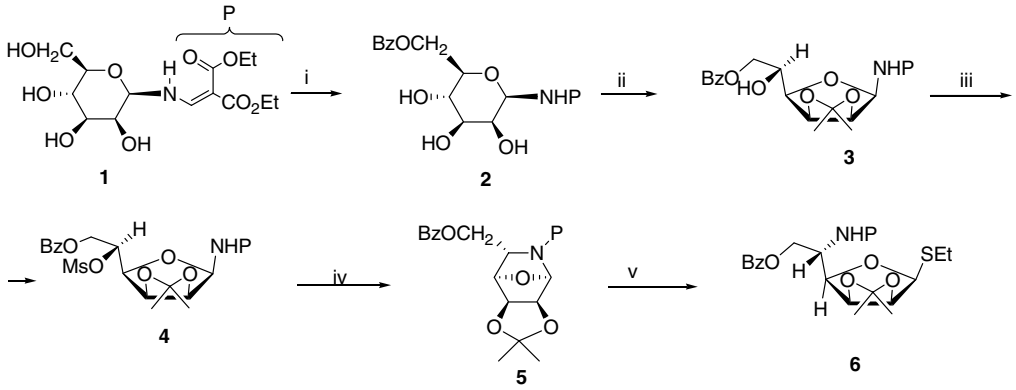
doi:10.1016/j.tetasy.2004.05.027

2. Results and discussion

The primary hydroxyl group of the inexpensive β-D-mannopyranosylenamine **1**[19] was regioselectively *O*-benzoylated (Scheme 1) by treatment with benzoyl chloride and pyridine at −40 °C for 24 h, to obtain **2** (36% yield). The chemical shifts of H-6a and H-6b (4.53 and 4.30 ppm, respectively) were indicative of the esterification.

Treatment of **2** with dimethoxypropane in acetone in the presence of 10-camphor sulfonic acid (CAS) at 60 °C for 1 h produced the 2,3-*O*-isopropylidene D-mannofuranosylenamine **3** in high yield. Compound **3** was *O*-mesylated by reaction with mesyl chloride in pyridine at rt for 24 h under argon to obtain the 5-*O*-mesyl derivative **4** in 82% yield. The furanoid structure of **3** and **4** was supported by NMR spectroscopic data (Table 1 and Experimental). Thus the $J_{3,4}$ value was in the range 3.4–3.6 Hz, suggesting a *cis*-relationship between the corresponding protons, which is possible in the furanoid structure but not in a pyranoid structure. The resonances for C-1, C-2, C-3, and C-4 in **3** and **4** were in the expected range for furanoid sugar derivatives, which is deshielded (5–12 ppm) as expected for pyranoid analogues.[20] In fact, these deshieldings are observed in the comparison of the data for **3** and **4** with the data for **2** (Table 1 and Experimental). Moreover, the resonance for H-5 in **4** was at 5.24, 0.9 ppm deshielded with respect to the signal for the same proton in **3**, indicating that esterification took place at position five, and consequently confirming the furanoid structure. The anomeric β configuration of **3** and **4** is supported by the formation of the azaanhydroderivative **5** (see below), which is only possible if the enamino group and the exocyclic sugar backbone are in a *cis*-relationship.

Although neither ring contraction nor anomeric equilibria have been described for glycohexopyranosylamines, we presume that in the acid medium, oxo-cation **16** is formed, which evolves to the key intermediate stabilized iminium cation **17**. On neutralization, the [3.3.0] bicyclic acetal **3** is preferentially formed. Small amounts of the [4.3.0] bicyclic acetal **18** were detected, but they evolved to **3** in the reaction medium (Scheme 2).

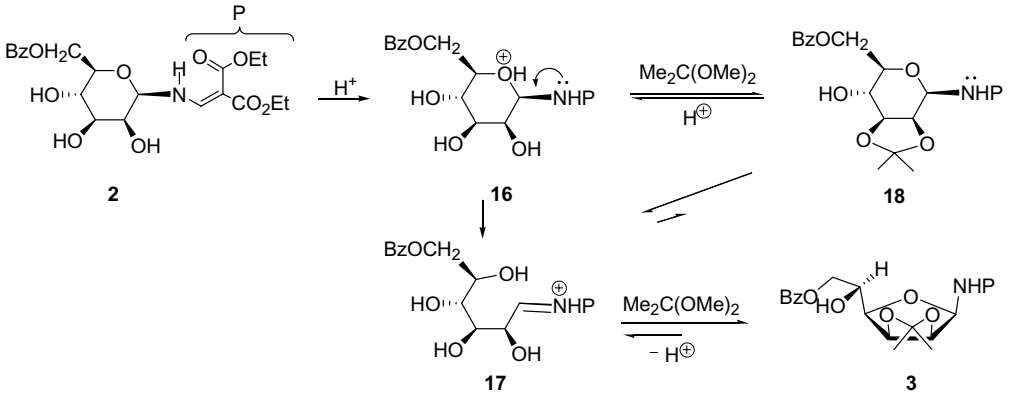


Scheme 1. Reagents and conditions: (i) ClBz/Py, −40 °C, 24 h; (ii) 2,2-dimethoxypropane, CAS, 60 °C, 1 h; (iii) ClMs/Py, rt, 24 h; (iv) NaOMe/DMF, 45 °C/20 mmHg, 8 h; (v) EtSH/Cl_2CH_2/PTSA, rt, 15 min.

Table 1. Selected NMR spectroscopic data (δ ppm, J Hz) for compounds **2**–**6** and **8**–**15** at 500 (^{1}H) and 125 (^{13}C) MHz

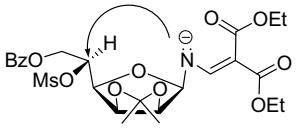
	Sugar ring										Enamino moiety			
	δ values							J^a values			δNH	δ=CH	δ=CH	δ=C
	H-1	H-2	H-4	H-5	C-1	C-4	C-5	1,2	3,4	4,5				
2[b]	4.93	3.74	3.54	3.54	85.3	66.1	75.6	—	—	—	9.39	8.09	158.9	91.0
3[c]	4.81	4.71	3.66	4.33	89.4	76.7	68.5	3.8	3.6	8.2	9.43	8.05	157.4	94.0
4[c]	4.82	4.75	3.92	5.24	89.4	76.0	76.3	3.9	3.4	7.5	9.44	8.01	157.1	94.5
5[b]	5.84	4.63	5.03	4.45	91.1	82.1	55.4	2.9	4.9	0.0	—	7.63	144.6	93.9
6[c]	4.66	4.80	3.68	4.07	87.7	80.2	58.3	4.0	3.5	8.5	9.54	8.16	160.0	90.8
8[c]	4.79	4.69	3.37	4.09	89.3	82.1	66.1	3.8	3.7	7.7	9.42	8.06	157.5	93.8
9[c]	4.83	4.28	3.45	3.40	83.9	73.7	73.2	2.4	6.6	9.0	9.34	8.06	158.0	93.2
10[b]	5.15	4.75	3.70	4.85–4.82	87.7	78.2	76.0	3.5	3.2	6.8	9.20	8.11	157.7	92.2
11[b]	5.76	4.57	4.65	4.19	92.9	85.4	52.1	2.8	5.0	0.0	—	7.52	144.4	92.0
12[c]	4.64	4.79	3.35	3.80	87.5	84.3	54.2	4.0	3.5	8.8	9.27	8.13	159.3	89.4
13[c]	4.62	4.79	3.35	3.80	87.7	84.1	54.5	4.0	3.4	8.9	9.27	8.13	159.1	89.4
14[c]	4.62	4.79	3.35	3.80	88.0	84.5	54.8	3.9	3.5	8.9	9.29	8.12	159.4	89.8
15[c]	4.71	4.89	3.33	3.86	90.8	84.4	54.3	4.0	3.5	9.0	9.30	8.23	159.4	89.6

[a] Only the values directly measured on the spectra are indicated.
[b] In DMSO-d_6.
[c] In $CDCl_3$.



Scheme 2. Mechanism of the formation of **3**.

Treatment of **4** with sodium methoxide in DMF at 40 °C and under reduced pressure for 8 h produced the anhydroazasugar derivative **5** in 73% yield. The reaction took place through the stabilized intermediate amide anion **19**,[2] which by internal nucleophilic displacement of the 5-OMs group afforded **5**. The ^{1}H NMR spectrum of **5** contained no signal for NH, and showed a singlet for the HC= of the enamino moiety (=CHNR$_2$) instead of the doublet (=CHNHR) of the spectrum of **4**. The signal for H-1 was strongly (1.02 ppm) shifted downfield, whereas the resonances for H-5 and C-5 were shifted upfield (0.79 and 20.9 ppm, respectively) as expected for the substitution of a sulfonyloxy group by an enamino group. The NMR data for the enamino moiety of **5** were similar to those previously described[4] for related *N*-protected anhydroazasugars. Very marked changes were observed in all the coupling constants of the sugar ring of **5**, in accordance with the conformational change by the formation of the tricyclic system.



19

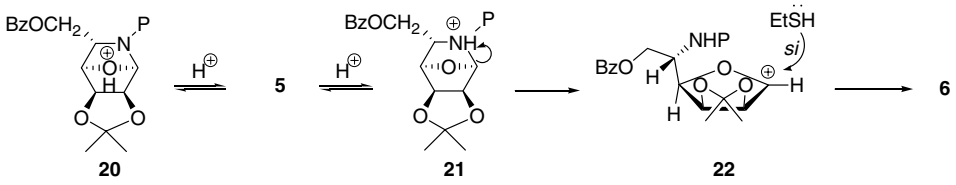
Reaction of **5** with ethanethiol in dichloromethane in the presence of *p*-toluenesulfonic acid (PTSA) at rt for 15 min produced ethyl α-L-*gulo* thiofuranoside **6**. The ^{1}H NMR spectrum of **6** showed again the signal for NH, and the resonance for *HC*= was a doublet; the data for the enamino moiety were close to those for **2**–**4** (Table 1 and Experimental). The chemical shift for the resonances of C-1 (87.7 ppm) was similar to that described for ethyl 1-thioglycopyranosides[20] and ethyl 1-thioglycofuranosides.[13] The ethylthio group was also evident from MS data and from the resonances of the S–CH$_2$ group.[13,18] An HMBC correlation spectrum[21] showed a 3-bond connection between *C*-1 and S-C*H*$_2$, and between *H*-1 and S-*C*H$_2$ groups.

For the assignment of the stereochemistry of C-1 in **6**, DPFGSE-NOE[22] experiments were performed. Such experiments were crucial in the case of H-4, since selective excitation of this proton revealed a strong NOE effect with H-1, similar to that observed with the vicinal H-3, showing a close proximity between these nuclei and thus suggesting that both protons should be on the same face of the sugar ring. Also in agreement with this configuration at C-1 is the observation of a small NOE contact between the methylene group of the aglycon and the *endo* methyl of the isopropylidene group.

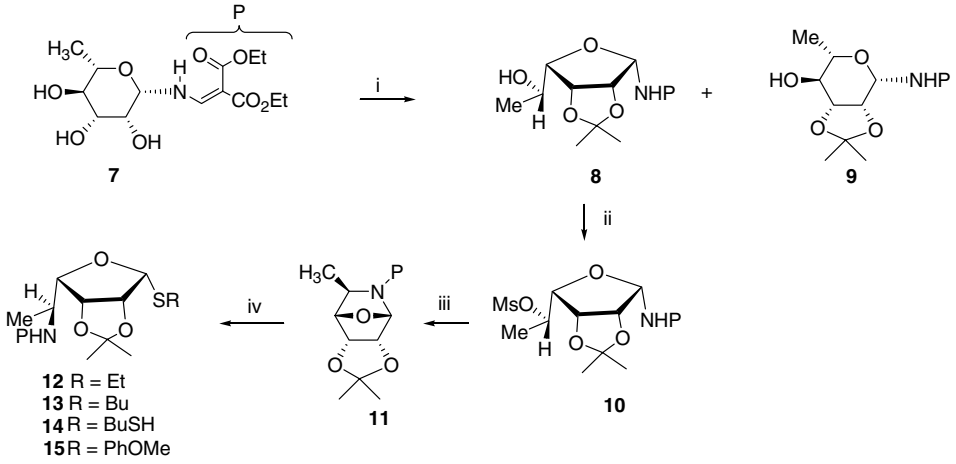
The formation of **6** is stereoselective with only the α-L anomer† being isolated. Under the reaction conditions, **5** can be protonated (Scheme 3) on the endocyclic oxygen atom (→ **20**) or on the nitrogen atom (→ **21**). The cleavage of the C1–N bond to form ion **22** is preferential with respect to the cleavage of the C1–O bond; as in the first case the *cis* [3.3.0] stable bicyclic system is retained. The conformation of the furanose ring of **22** is close to ^{0}T$_1$ ⇌ E$_1$ ⇌ ^{2}T$_1$, while the attack of the ethanethiol on *si* face of **21** produces **6**. The presence of the isopropylidene group determines the course of the reaction; the [3.3.0] ring favors the cleavage of the C–N bond, whereas in absence of the isopropylidene group, the cleavage of the C–O bond is predominant.[18]

Similarly with the aim of obtaining information from another glycosylenamine with the same relative configuration and to easily form a 2,3-isopropylidene derivative, we started from the β-L-rhamnopyranosylenamine **7**[19] (Scheme 4). This compound has no primary hydroxyl group, and consequently the first low-yielding benzoylation is not necessary, thus increasing the overall yield. Reaction of **7** with dimethoxypropane under the same conditions described above for **2** afforded **8** (major) and **9** (minor). When the pyranosyl derivative **9** was placed in acetone, CAS produced a 1:1 mixture of **8** and **9**. The spectroscopic data of **8** were very close to those for **3** (Table 1 and Experimental) as the furanoid moiety of both compounds are enantiomers. In the case of **9**, the measured vicinal coupling constants of the sugar ring, together with a shielding[20] in the resonances of the carbons of the same ring, confirmed the pyranoid structure.

† The anomeric configurational symbol changes due to the inversion at C-5.



Scheme 3.



Scheme 4. Reagents and conditions: (i) 2,2-dimethoxypropane, CAS, 60 °C, 1 h; (ii) ClMs/Py, rt, 24 h; (iii) NaOMe/DMF, 45 °C/20 mmHg, 15 min; (iv) RSH/Cl_2CH_2/PTSA, rt, 15 min.

Treatment of **8** with mesyl chloride gave **10**, which by reaction with sodium methoxide in DMF produced the anhydrosugar derivative **11** in high yield. The formation of **10** involves (Table 1) a considerable deshielding in the resonance for H-5, while compound **11** had similar structural supports to those discussed above for **5**.

Finally, reaction of **10** with ethanethiol, 1-butanethiol, 1,4-butanedithiol, and 4-methoxythiophenol in the presence of PTSA yielded the corresponding furanoid alkyl **12**–**14** or 4-methoxyphenyl **15** 1-thiofuranoside. In the case of the 1,4-butanedithiol, the monoglycosyl derivative **14** was the only product isolated. The chemical shifts and the coupling constants for the sugar ring and for the enamino moiety of **12**–**15** were very close (Table 1 and Experimental) to the corresponding data for **6**, and confirmed the proposed structures. The anomeric configuration of **12** and **15** (Fig. 1) was established through 1D NOESY experiments similar to those discussed above for **6**. The NOE contact H-4 and H-1 was determinant; an NOE between S–CH_2 and the *endo* methyl of the isopropylidene group for **12** and a NOE between aromatic protons (*ortho*) and CH═ of the enamino moiety for **15**, were also observed.

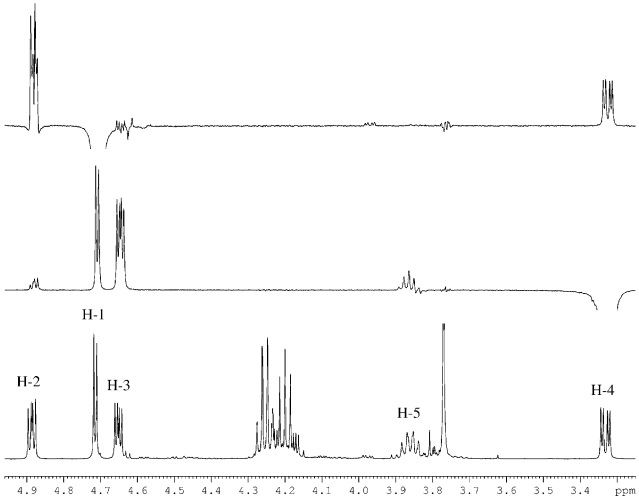


Figure 1. ^{1}H NMR and DPFGSE-NOE spectra of **15**.

3. Conclusion

In conclusion, the pyranoid ring of glycohexopyranosylenamines can be transformed into a furanoid ring, if the sugar configuration permits the formation of a *cis*-2,3-*O*-isopropylidene derivative (D-manno and L-rhamno configuration as examples). The furanoid glycohexofuranosylenamines, which have the enamino moiety and the exocyclic sugar backbone in a *cis*-relationship (**3** and **8**), can be transformed in three steps into alkyl (aryl) 1-thioglycofuranosides of 5-aminosugars **6** and **12**–**15**. The key intermediate of this transformation is an anhydroazasugar derivative **5** or **11**. Herein the dialkoxycarbonylvinyl group was used to protect the amino group and to stabilize a negative charge in the formation of the azaanhydrocompounds. The dialkoxycarbonylvinylamino group stabilized the positive charge in the ring contraction reaction. All the reactions are highly stereoselective.

4. Experimental

4.1. General methods

Melting points were determined with a Gallenkamp apparatus and are uncorrected. A Perkin–Elmer Model 141 MC polarimeter, 1-cm tubes, and solutions in CH_2Cl_2, at 589 nm, were used for measurement of specific rotations. IR spectra were recorded for KBr discs on a Bomen Michelson MB-120 FTIR spectrophotometer. Mass spectra (EI, CI, and FAB) were recorded with a Kratos MS-80RFA or a Micromass AutoSpecQ instrument with a resolution of 1000 or 60,000 (10% valley definition). For the FAB spectra, ions were produced by a beam of xenon atoms (6–7 keV), using 3-nitrobenzyl alcohol or thioglycerol as matrix and NaI as salt. TLC was performed on silica gel HF_{254}, with detection by UV light or charring with H_2SO_4. Silica gel 60 (Merck, 70–230 and 230–400 mesh) was used for preparative chromatography.

NMR experiments were recorded on a Bruker AMX or Avance AV 500 spectrometer (500.13 MHz for ^1H and 125.75 MHz for ^{13}C). Sample concentrations were typically in the range 10–15 mg per 0.6 mL of $CDCl_3$. Chemical shifts are given in ppm, using the residual protonated solvent signal as reference. ^1H and ^{13}C assignments were confirmed by 2D conventional COSY, HMQC, or HSQC and HMBC experiments. For the HMQC experiment, the null time following the BIRD pulse was 400 ms. The HMBC experiments were optimized for long-range coupling constants of 10 Hz. 1D NOESY experiments were carried out on a 5 mm inverse detection probe operating at 303 K, by using the double-pulsed field gradient spin-echo technique (DPFGSE-NOE).[22] A mixing time of 400 ms, a recycle delay of 2 s, and 1024 transients per spectrum, were used in all cases. Selective inversions were performed by using Gaussian-shaped soft pulses (50 ms).

4.2. 6-*O*-Benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-mannopyranosylamine, 2

To a stirred solution of **1** (1.03 g, 2.88 mmol) in pyridine (8 mL) at −40 °C was gradually added benzoyl chloride (680 μL, 5.82 mmol). The mixture was kept for 24 h, the reaction controlled by TLC (CH_2Cl_2/MeOH, 15:1) and then 5 mL of water added. The mixture was twice evaporated to dryness with toluene. The residue was purified by column chromatography (CH_2Cl_2/MeOH, 30:1) to give an amorphous solid. Yield 36%; $[\alpha]_D^{22} = +52$ (*c* 1.0, MeOH); FABMS *m/z* 476 [(M+Na)$^+$]; IR 3524, 3385, 2982, 2901, 1703, 1640, 1593, 1452, 1377, 1289, 1248, 1092, 1022, 868, 797, 712 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 9.39 (dd, 1H, $J_{NH,1} = 8.9$, $J_{NH,HC} = 14.1$, NH), 8.09 (d, 1H, HC=), 7.96–7.50 (m, 5H, Ar), 5.36 (d, 1H, $J_{2,OH} = 5.3$, O*H*-H2), 5.15 (d, 1H, $J_{4,OH} = 3.9$, O*H*-H4), 5.06 (d, 1H, $J_{3,OH} = 5.3$, O*H*-H3), 4.93 (d, 1H, H-1), 4.53 (d, 1H, $J_{6a,6b} = 11.8$, H-6a), 4.30 (dd, 1H, $J_{5,6b} = 5.3$, H-6b), 4.09, 4.03 (each q, each 2H, $J_{H,H} = 7.1$, 2CH_2CH$_3$), 3.74 (m, 1H, H-2), 3.54 (m, 2H, H-4,H-5), 3.41 (m, 1H, H-3), 1.18, 1.15 (each t, each 3H, 2CH$_2$CH_3); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 167.4 (C=O benzoyl), 165.8, 164.9 (2C=O), 158.9 (CH=), 133.3–128.8 (Ar), 91.0 (C=), 85.3 (C-1), 75.6 (C-5), 73.4 (C-3), 69.9 (C-2), 66.1 (C-4), 64.4 (C-6), 59.3, 59.1 (2*C*H$_2$CH$_3$), 14.3, 14.2 (2CH$_2$*C*H$_3$); Anal Calcd for $C_{21}H_{27}NO_{10}$: C, 55.62; H, 6.00; N, 3.09. Found: C, 55.25; H, 5.91; N, 3.18.

4.3. Preparation of compounds 3, 8, and 9

A solution of the corresponding compound **2** or **7** (0.312 mmol), dimethoxypropane dimethyl acetal (0.624 mmol), and CAS (0.027 mmol) in acetone (1 mL) was stirred at 60 °C for 1 h. The solution was poured into cool aq $NaHCO_3$ (saturated), extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated. From **2**, the residue was purified by column chromatography (CH_2Cl_2/MeOH 60:1) to give compound **3**. From **7**, the residue was purified by column chromatography (diethyl ether) to give compounds **8** and **9**. Compound **9** was treated with acetone/CAS at 60 °C to yield a mixture 1:1 of **8** and **9**.

4.3.1. 6-*O*-Benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-β-D-mannofuranosylamine, 3. Amorphous solid. Yield 85%; $[\alpha]_D^{22} = +88$ (*c* 0.9, CH_2Cl_2); FABMS *m/z* 516 [(M+Na)$^+$]; IR 3466, 3345, 3304, 2982, 2945, 1717, 1665, 1605, 1452, 1377, 1269, 1225, 1105, 1032, 806, 714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.43 (dd, 1H, $J_{NH,1} = 9.3$, $J_{NH,HC} = 13.6$, NH), 8.05 (d, 1H, HC=), 8.09–7.42 (m, 5H, Ar), 4.93 (dd, 1H, $J_{2,3} = 6.0$, $J_{3,4} = 3.6$, H-3), 4.81 (dd, 1H, $J_{1,2} = 3.8$, H-1), 4.71 (dd, 1H, H-2), 4.65 (dd, 1H, $J_{5,6a} = 2.9$, $J_{6a,6b} = 11.8$, H-6a), 4.44 (dd, 1H, $J_{5,6b} = 5.9$, H-6b), 4.33 (m, 1H, H-5), 4.26, 4.19 (each q, each 2H, $J_{H,H} = 7.1$, 2CH_2CH$_3$), 3.66 (dd, 1H, $J_{4,5} = 8.2$, H-4), 1.63, 1.40 (each s, each 3H, 2(CH_3)$_2$C), 1.33, 1.28 (each t, each 3H, 2CH$_2$CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.8 (2C=O benzoyl), 167.0, 165.7 (2C=O), 157.4 (CH=), 133.2–128.4 (Ar), 113.9 (*C*(CH$_3$)$_2$), 94.0 (C=), 89.4 (C-1), 80.3 (C-3), 79.0 (C-2), 76.7 (C-4), 68.5 (C-5), 66.9 (C-6), 60.1, 59.9 (2*C*H$_2$CH$_3$), 25.9, 24.8 [(*C*H$_3$)$_2$C], 14.4, 14.3 (2CH$_2$*C*H$_3$); Anal Calcd for $C_{24}H_{31}NO_{10}$: C, 58.41; H, 6.33; N, 2.84. Found: C, 58.60; H, 6.33; N, 2.85.

4.3.2. *N*-(2,2-Diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-β-L-rhamnofuranosylamine, 8. Amorphous solid. Yield 55%; $[\alpha]_D^{24} = -81$ (*c* 1.0, CH_2Cl_2); FABMS *m/z* 396 [(M+Na)$^+$]; IR 3384, 3306, 2984, 2938, 1697, 1669, 1614, 1449, 1384, 1324, 1261, 1226, 1172, 1044, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.42 (dd, 1H, $J_{NH,1} = 9.3$, $J_{NH,HC=} = 13.6$, NH), 8.06 (d, 1H, HC=), 4.87 (dd, 1H, $J_{2,3} = 6.1$, $J_{3,4} = 3.7$, H-3), 4.79 (dd, 1H, $J_{1,2} = 3.8$, H-1), 4.69 (dd, 1H, H-2), 4.26, 4.19 (each q, each 2H, $J_{H,H} = 7.0$, 2CH_2CH$_3$), 4.09 (m, 1H, H-5), 3.37 (dd, 1H, $J_{4,5} = 7.7$, H-4), 2.09 (d, 1H, $J_{5,OH} = 5.2$, O*H*-H5), 1.60, 1.39 (each s, each 3H, (CH_3)$_2$C), 1.33 (d, 3H, $J_{5,6} = 7.7$, H-6), 1.33, 1.29 (each t, each 3H, 2CH$_2$CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.9, 165.9 (2C=O), 157.5 (CH=), 113.8 (*C*(CH$_3$)$_2$), 93.8 (C=), 89.3 (C-1),

82.1 (C-4), 80.3 (C-3), 79.3 (C-2), 66.1 (C-5), 60.1, 60.0 ($2CH_2CH_3$), 25.9, 24.9 [$(CH_3)_2C$], 20.7 (C-6), 14.5, 14.4 ($2CH_2CH_3$); Anal Calcd for $C_{17}H_{27}NO_8$: C, 54.68; H, 7.29; N, 3.75. Found: C, 54.76; H, 7.47; N, 3.81.

4.3.3. *N*-(2,2-Diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-β-L-rhamnopyranosylamine, 9. Amorphous solid. Yield 45%; $[\alpha]_D^{24} = -58$ (*c* 1.0, CH_2Cl_2); FABMS *m/z* 396 [(M+Na)$^+$]; IR 3449, 3385, 3298, 2984, 2937, 1678, 1603, 1449, 1379, 1247, 1023, 804 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (dd, 1H, $J_{NH,1} = 8.9$, $J_{NH,HC=} = 13.6$, NH), 8.06 (d, 1H, HC=), 4.83 (dd, 1H, $J_{1,2} = 2.4$, H-1), 4.28 (dd, 1H, $J_{2,3} = 5.8$, H-2), 4.28–4.17 (m, 4H, $2CH_2CH_3$), 4.10 (dd, 1H, $J_{3,4} = 6.6$, H-3), 3.45 (ddd, 1H, $J_{4,5} = 9.0$, $J_{4,OH} = 3.8$, H-4), 3.40 (dq, 1H, $J_{5,6} = 6.1$, H-5), 2.40 (d, 1H, O*H*-H4), 1.56, 1.39 (each s, each 3H, $(CH_3)_2C$), 1.33, 1.29 (each t, each 3H, $J_{H,H} = 7.0$, $2CH_2CH_3$), 1.33 (d, 3H, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.3, 165.8 (2C=O), 158.0 (CH=), 110.5 ($C(CH_3)_2$), 93.2 (C=), 83.9 (C-1), 79.3 (C-2), 73.7 (C-3), 73.2 (C-4), 73.0 (C-5), 59.9, 59.8 ($2CH_2CH_3$), 27.6, 26.1 ($(CH_3)_2C$), 17.7 (C-6), 14.2, 14.0 ($2CH_2CH_3$); HREIMS *m/z* obsd 373.1735 calcd for $C_{17}H_{27}NO_8$ 373.1737.

4.4. Preparation of compounds 4 and 10

Into a cooled (0 °C) stirred solution of the corresponding compound **3** or **8** (0.894 mmol) in pyridine (3.1 mL) under argon, mesyl chloride (248 μL, 3.12 mmol) was dropped. The mixture was stirred at rt for 24 h and the reaction controlled by TLC (CH_2Cl_2/MeOH, 100:1). The solution was poured into ice-water and extracted with CH_2Cl_2; the organic layer was separated, washed with 1 M sulfuric acid, satd aq $NaHCO_3$, and water, dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified as described.

4.4.1. 6-*O*-Benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-5-*O*-mesyl-β-D-mannofuranosylamine, 4. Column chromatography (CH_2Cl_2) yields an amorphous solid, 82%; $[\alpha]_D^{20} = +75$ (*c* 0.8, CH_2Cl_2); FABMS *m/z* 594 [(M+Na)$^+$]; IR 3297, 2984, 2940, 1725, 1665, 1605, 1454, 1371, 1267, 1103, 802, 714 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (dd, 1H, $J_{NH,1} = 9.4$, $J_{NH,HC=} = 13.5$, NH), 8.01 (d, 1H, HC=), 8.09–7.42 (m, 5H, Ph), 5.24 (ddd, 1H, $J_{4,5} = 7.5$, $J_{5,6a} = 2.3$, $J_{5,6b} = 6.2$, H-5), 4.87 (m, 1H, H-6a), 4.86 (m, 1H, H-3), 4.82 (dd, 1H, $J_{1,2} = 3.9$, H-1), 4.75 (dd, 1H, $J_{2,3} = 5.9$, H-2), 4.51 (dd, 1H, $J_{6a,6b} = 12.7$, H-6b), 4.27, 4.19 (each m, each 2H, $2CH_2CH_3$), 3.92 (dd, 1H, $J_{3,4} = 3.4$, H-4), 3.09 (s, 3H, Ms), 1.64, 1.40 (each s, each 3H, $(CH_3)_2$), 1.34, 1.29 (each t, each 3H, $J_{H,H} = 7.0$, $2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 167.7 (C=O), 165.9, 165.5 (2C=O), 157.1 (CH=), 133.2–128.4 (Ph), 114.2 ($C(CH_3)_2$), 94.5 (C=), 89.4 (C-1), 79.3 (C-3), 78.8 (C-2), 76.3 (C-5), 76.0 (C-4), 63.8 (C-6), 60.1, 59.9 ($2CH_2CH_3$), 38.7 (Ms), 25.8, 24.9 ($(CH_3)_2C$), 14.3, 14.2 ($2CH_2CH_3$); Anal Calcd for $C_{25}H_{33}NO_{12}$ S: C, 52.53; H, 5.82; N, 2.45. Found: C, 52.29; H, 5.81; N, 2.46.

4.4.2. *N*-(2,2-Diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-5-*O*-mesyl-β-L-rhamnofuranosylamine, 10. Column chromatography (AcOEt/hexane, 1:2) yields an amorphous solid, 90%; $[\alpha]_D^{24} = -40$ (*c* 0.9, CH_2Cl_2); FABMS *m/z* 474 [(M+Na)$^+$]; IR 3383, 3330, 2995, 2948, 1705, 1675, 1607, 1458, 1356, 1237, 812 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 50 °C) δ 9.20 (dd, 1H, $J_{NH,1} = 9.2$, $J_{NH,HC=} = 13.6$, NH), 8.11 (d, 1H, HC=), 5.15 (dd, 1H, $J_{1,2} = 3.5$, H-1), 4.85–4.82 (m, 2H, H-3, H-5), 4.75 (dd, 1H, $J_{2,3} = 6.0$, H-2), 4.13, 4.07 (each q, each 2H, $J_{H,H} = 7.0$, $2CH_2CH_3$), 3.70 (dd, 1H, $J_{3,4} = 3.2$, $J_{4,5} = 6.8$, H-4), 3.18 (s, 3H, Ms), 1.47, 1.32 [each s, each 3H, $(CH_3)_2C$], 1.42 (d, 3H, $J_{5,6} = 6.0$, H-6), 1.21, 1.20 (each t, each 3H, $2CH_2CH_3$); ^{13}C NMR (125.7 MHz, DMSO-d_6, 50 °C) δ 167.2, 164.7 (2C=O), 157.7 (CH=), 112.4 [$C(CH_3)_2$], 92.2 (C=), 87.7 (C-1), 79.1 (C-3), 78.5 (C-2), 78.2 (C-4), 76.0 (C-4), 59.4, 59.2 ($2CH_2CH_3$), 38.0 (Ms), 25.6, 24.6 [$(CH_3)_2C$], 18.7 (C-6), 14.2 ($2CH_2CH_3$); Anal Calcd for $C_{18}H_{29}NO_{10}S$: C, 47.88; H, 6.47; N, 3.10; S, 7.10. Found: C, 47.75; H, 6.44; N, 3.18; S, 6.96.

4.5. Preparation of compounds 5 and 11

To a stirred solution of the corresponding mesyl compound **4** or **10** (0.27 mmol) in DMF (5.0 mL) at 40 °C and 20 mmHg, sodium methoxide (16 mg, 0.27 mmol) was added. The reaction was stirred for 8 h for **5** and 15 min for **11**. The mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified as described.

4.5.1. 1,5-Anhydro-6-*O*-benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-α-L-gulofuranosylamine, 5. Column chromatography (CH_2Cl_2/MeOH, 100:1) yields an amorphous solid, 73%; $[\alpha]_D^{24} = +109$ (*c* 1.1, CH_2Cl_2); FABMS *m/z* 498 [(M+Na)$^+$]; IR 3063, 2982, 2936, 1721, 1686, 1597, 1447, 1383, 1267, 714 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 60 °C) δ 7.97–7.50 (m, 5H, Ar), 7.63 (br s, 1H, HC=), 5.84 (br s, 1H, H-1), 5.03 (d, 1H, $J_{3,4} = 4.9$, H-4), 4.78 (dd, 1H, $J_{2,3} = 8.1$, H-3), 4.63 (dd, 1H, $J_{1,2} = 2.9$, H-2), 4.45 (m, 1H, H-5), 4.19 (br s, 2H, H-6a, H-6b), 4.14–4.04 (m, 4H, $2CH_2CH_3$), 1.51, 1.31 (each s, each 3H, [$(CH_3)_2C$]), 1.18, 1.16 (each t, each 3H, $J_{H,H} = 7.0$, $2CH_2CH_3$); ^{13}C NMR (125.7 MHz, DMSO-d_6, 60 °C) δ 165.9 (C=O), 165.0 (2C=O), 144.6 (CH=), 133.1–128.4 (Ar), 118.8 [$C(CH_3)_2$], 93.9 (C=), 91.1 (C-1), 82.1 (C-4), 80.5 (C-2), 75.9 (C-3), 61.2 (C-6), 59.8, 59.1 ($2CH_2CH_3$), 55.4 (C-5), 25.0, 24.9 [$(CH_3)_2C$], 13.9, 13.6 ($2CH_2CH_3$); Anal Calcd for $C_{24}H_{29}NO_9$: C, 60.62; H, 6.15; N, 2.95. Found: C, 60.24; H, 6.09; N, 2.92.

4.5.2. 1,5-Anhydro-6-deoxy-*N*-(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-α-D-gulofuranosylamine, 11. Column chromatography (ether/hexane, 4:1) yields an amorphous solid, 77%; $[\alpha]_D^{24} = -17$ (*c* 1.0, CH_2Cl_2); FABMS *m/z* 378 [(M+Na)$^+$]; IR, 2988, 2936, 1690, 1597, 1420, 1374, 1269, 740 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 7.52 (br s, 1H, HC=), 5.76 (br s, 1H,

H-1), 4.70 (dd, 1H, $J_{3,4} = 5.0$, $J_{4,5} = 8.0$, H-4), 4.65 (m, 1H, H-3), 4.57 (dd, 1H, $J_{1,2} = 2.8$, $J_{2,3} = 8.5$, H-2), 4.19 (m, 1H, H-5), 4.11–4.06 (m, 4H, $2CH_2CH_3$), 1.50, 1.28 (each s, each 3H, $[(CH_3)_2C]$), 1.21, 1.17 (each t, each 3H, $J_{H,H} = 7.0$, $2CH_2CH_3$), 0.94 (d, 3H, $J_{5,6} = 6.0$, H-6); ^{13}C NMR (125.7 MHz, DMSO-d_6, 30 °C) δ 166.6, 166.4 (2C=O), 144.4 (CH=), 118.9 [$C(CH_3)_2$], 92.7 (C-1), 92.0 (C=), 85.4 (C-4), 80.0 (C-2), 76.2 (C-3), 60.0, 59.3 ($2CH_2CH_3$), 52.1 (C-5), 25.3, 25.2 [$(CH_3)_2C$], 15.7 (C-6), 14.4, 14.2 ($2CH_2CH_3$). HRCIMS m/z obsd 356.1689 calcd for $C_{17}H_{25}NO_7$ 356.1709.

4.6. Preparation of compounds 6, 12–14

To a stirred solution of the corresponding compound **5** or **11** (0.270 mmol) in dry CH_2Cl_2 (4.0 mL), over 3 Å molecular sieves, ethanethiol (**5** → **6**), and (**11** → **12**), 1-butanethiol, (**11** → **13**), 1,4-butanedithiol, (**11** → **14**), and 4-methoxythiophenol (**11** → **15**) (6.775 mmol), and PTSA (0.393 mmol) were added. The reaction was controlled by TLC (CH_2Cl_2/MeOH, 100:1). The solution was poured into a stirred mixture of ice and satd aq $NaHCO_3$, extracted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The residue was purified as indicated.

4.6.1. Ethyl 6-*O*-benzoyl-5-deoxy-5-*N*-(2,2-diethoxycarbonylvinylamine)-2,3-*O*-isopropylidene-1-thio-α-L-gulofuranoside, 6. Column chromatography (CH_2Cl_2, CH_2Cl_2/MeOH, 100:1). Yield 73% as amorphous solid; $[\alpha]_D^{23} = +37$ (*c* 1.5, CH_2Cl_2); EIMS m/z 537 M^+; IR 3265, 2980, 2934, 2872, 1723, 1656, 1608, 1451, 1379, 1270, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.54 (dd, 1H, $J_{NH,5} = 9.0$, $J_{NH,HC=} = 14.0$, NH), 8.16 (d, 1H, HC=), 8.04–7.42 (m, 5H, Ph), 4.80 (dd, 1H, $J_{1,2} = 4.0$, $J_{2,3} = 6.0$, H-2), 4.71 (dd, 1H, $J_{3,4} = 3.5$, H-3), 4.69 (m, 1H, H-6a), 4.66 (d, 1H, H-1), 4.47 (dd, 1H, $J_{5,6b} = 4.0$, $J_{6a,6b} = 12.0$, H-6b), 4.22, 4.16 (each q, each 2H, $J_{H,H} = 7.5$, $2CH_2CH_3$), 4.07 (m, 1H, H-5), 3.68 (dd, 1H, $J_{4,5} = 8.5$, H-4), 2.67 (m, 2H, SCH_2), 1.51 (s, 3H, $(CH_3)_2C$), 1.31 (t, 3H, CH_2CH_3), 1.28 (s, 3H, $(CH_3)_2C$), 1.25 (t, 6H, CH_2CH_3, SCH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.3 (C=O benzoyl), 166.2, 165.8 (2C=O), 160.0 (CH=), 133.6–128.6 (Ar), 113.7 ($C(CH_3)_2$), 90.8 (C=), 87.7 (C-1), 82.8 (C-2), 80.2 (C-4), 79.8 (C-3), 64.5 (C-6), 60.0, 59.7 ($2CH_2CH_3$), 58.3 (C-5), 26.6 (SCH_2CH_3), 25.9, 24.9 [$(CH_3)_2C$], 15.5 (SCH_2CH_3), 14.6, 14.5 ($2CH_2CH_3$); HREIMS m/z obsd 537.2035 calcd for $C_{26}H_{35}NO_9S$ 537.2033.

4.6.2. Ethyl 5,6-di-deoxy-5-*N*-(2,2-diethoxycarbonylvinylamine)-2,3-*O*-isopropylidene-1-thio-α-D-gulofuranoside, 12. Column chromatography (CH_2Cl_2, CH_2Cl_2/MeOH, 100:1). Yield 73% as amorphous solid; $[\alpha]_D^{24} = -49$ (*c* 0.9, CH_2Cl_2); FABMS m/z 440 [(M+Na)$^+$]; IR 3331, 2984, 2926, 2862, 1701, 1654, 1611, 1424, 1364, 1277, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.27 (dd, 1H, $J_{NH,5} = 8.0$, $J_{NH,HC} = 14.0$, NH), 8.13 (d, 1H, HC=), 4.79 (m, 1H, H-2), 4.64 (d, 1H, $J_{1,2} = 4.0$, H-1), 4.62 (dd, 1H, $J_{3,4} = 3.5$, H-3), 4.23, 4.17 (each q, each 2H, $J_{H,H} = 7.1$, $2CH_2CH_3$), 3.80 (m, 1H, H-5), 3.35 (dd, 1H, $J_{4,5} = 8.8$, H-4), 2.68 (m, 2H, SCH_2CH_3), 1.53, 1.32 (each s, each 3H, $[(CH_3)_2C]$, 1.38 (d, 3H, $J_{5,6} = 6.4$, H-6), 1.34, 1.28 (each t, each 3H, $2CH_2CH_3$), 1.27 (t, 3H, $J_{H,H} = 7.5$, SCH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.5, 166.0 (2C=O), 159.3 (CH=), 113.2 ($C(CH_3)_2$), 89.4 (C=), 87.5 (C-1), 84.3 (C-4), 82.6 (C-2), 79.9 (C-3), 59.7, 59.4 ($2CH_2CH_3$), 54.5 (C-5), 29.0 (SCH_2CH_3), 25.8, 25.0 [$(CH_3)_2C$], 17.3 (C-6), 15.4 (SCH_2CH_3), 14.4, 14.3 ($2CH_2CH_3$); HREIMS m/z obsd 417.1828 calcd for $C_{19}H_{31}NO_7S$ 417.1821.

4.6.3. Buthyl 5,6-di-deoxy-5-*N*-(2,2-diethoxycarbonylvinylamine)-2,3-*O*-isopropylidene-1-thio-α-D-gulofuranoside, 13. Column chromatography (CH_2Cl_2, CH_2Cl_2/MeOH, 100:1). Yield 65% as amorphous solid; $[\alpha]_D^{24} = -132$ (*c* 1.0, CH_2Cl_2); FABMS m/z 468 [(M+Na)$^+$]; IR 3296, 2984, 2930, 2859, 2149, 1701, 1655, 1609, 1429, 1375, 1260, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.27 (dd, 1H, $J_{NH,5} = 9.0$, $J_{NH,HC=} = 14.1$, NH), 8.13 (d, 1H, HC=), 4.79 (dd, 1H, $J_{1,2} = 4.0$, $J_{2,3} = 5.9$, H-2), 4.63 (dd, 1H, $J_{3,4} = 3.4$, H-3), 4.62 (d, 1H, H-1), 4.23 (q, 2H, $J_{H,H} = 7.1$, CH_2CH_3), 4.18 (m, 2H, CH_2CH_3), 3.80 (m, 1H, H-5), 3.35 (dd, 1H, $J_{4,5} = 8.9$, H-4), 2.66 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.58 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.35 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.52, 1.32 (each s, each 3H, $(CH_3)_2C$), 1.37 (d, 3H, $J_{5,6} = 6.8$, H-6), 1.33, 1.27 (each t, each 3H, $2CH_2CH_3$), 0.87 (t, 3H, $J_{H,H} = 7.4$, $SCH_2CH_2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.4, 166.0 (2C=O), 159.1 (CH=), 113.2 [$C(CH_3)_2$], 89.4 (C=), 87.7 (C-1), 84.1 (C-4), 82.6 (C-2), 79.9 (C-3), 59.6, 59.4 ($2CH_2CH_3$), 54.5 (C-5), 32.2 (SCH_2CH_2), 32.0 (SCH_2), 21.7 ($SCH_2CH_2CH_2$), 25.8, 24.9 [$(CH_3)_2C$], 17,3 (C-6), 14.4, 14.3 ($2CH_2CH_3$), 13.5 ($SCH_2CH_2CH_2CH_3$); HREIMS m/z obsd 445.2135 calcd for $C_{21}H_{35}NO_7S$ 445.2134.

4.6.4. 4-Buthylthio 5,6-di-deoxy-5-*N*-(2,2-diethoxycarbonylvinylamine)-2,3-*O*-isopropylidene-1-thio-α-D-gulofuranoside, 14. Column chromatography (CH_2Cl_2, CH_2Cl_2/MeOH, 100:1). Yield 64% as amorphous solid; $[\alpha]_D^{24} = -56$ (*c* 1.0, CH_2Cl_2); FABMS m/z 500 [(M+Na)$^+$]; IR 3304, 2988, 2933, 2853, 2147, 1684, 1654, 1616, 1426, 1374, 1283, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.29 (dd, 1H, $J_{NH,5} = 8.0$, $J_{NH,HC=} = 14.0$, NH), 8.12 (d, 1H, HC=), 4.79 (dd, 1H, $J_{1,2} = 3.9$, $J_{2,3} = 6.0$, H-2), 4.63 (dd, 1H, $J_{3,4} = 3.5$, H-3), 4.62 (d, 1H, H-1), 4.22 (q, 2H, $J_{H,H} = 7.1$, CH_2CH_3), 4.17 (m, 2H, CH_2CH_3), 3.80 (m, 1H, H-5), 3.35 (dd, 1H, $J_{4,5} = 8.9$, H-4), 2.67 (m, 2H, $SCH_2CH_2CH_2CH_2SH$), 2.50 (m, 2H, $SCH_2CH_2CH_2CH_2SH$), 1.73–1.69 (m, 4H, $SCH_2CH_2H_2CH_2SH$), 1.52 (s, 3H, $(CH_3)_2C$), 1.38 (d, 3H, $J_{5,6} = 6.7$, H-6), 1.34 (t, 3H, $2CH_2CH_3$), 1.32 (s, 3H, $(CH_3)_2C$), 1.29 (t, 3H, $2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.7, 166.4 (2C=O), 159.4 (CH=), 113.5 [$C(CH_3)_2$], 89.8 (C=), 88.0 (C-1), 84.5 (C-4), 82.8 (C-2), 80.1 (C-3), 59.9, 59.7 ($2CH_2CH_3$), 54.8 (C-5), 33.1 (SCH_2CH_2), 32.0 (SCH_2), 29.1 ($SCH_2CH_2CH_2$), 26.1, 25.2 [$(CH_3)_2C$], 24.3 ($SCH_2CH_2CH_2CH_2SH$), 17.5

(C-6), 14.7, 14.6 ($2CH_2CH_3$); HREIMS m/z obsd 477.1848 calcd for $C_{21}H_{35}NO_7S_2$ 477.1855.

4.6.5. (4-Methoxy)phenyl 5,6-di-deoxy-5-*N*-(2,2-diethoxycarbonylvinylamine)-2,3-*O*-isopropylidene-1-thio-α-D-gulofuranoside, 15. Amorphous solid. Yield 40%; $[\alpha]_D^{22} = +42$ (c 1.3, CH_2Cl_2); FABMS m/z 518 [(M+Na)$^+$]; IR 3433, 2984, 2936, 1648, 1603, 1489, 1381, 1279, 1242, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (dd, 1H, $J_{NH,5} = 7.5$, $J_{NH,HC=} = 14.0$, NH), 8.23 (d, 1H, HC=), 7.48–6.77 (m, 4H, Ar), 4.89 (dd, 1H, $J_{1,2} = 4.0$, $J_{2,3} = 6.0$, H-2), 4.71 (d, 1H, H-1), 4.65 (dd, 1H, $J_{3,4} = 3.5$, H-3), 4.23–4.20 (each q, each 2H, $J_{H,H} = 7.0$, $2CH_2CH_3$), 3.86 (m, 1H, H-5), 3.77 (s, 3H, OMe), 3.33 (dd, 1H, $J_{4,5} = 9.0$, H-4), 1.58, 1.35 (each s, each 3H, [$(CH_3)_2$C]), 1.39 (d, 3H, $J_{5,6} = 6.5$, H-6), 1.35, 1.28 (each t, each 3H, $2CH_2CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 169.5, 166.1 (2C=O), 159.7–114.5 (Ar), 159.4 (CH=), 113.5 [$C(CH_3)_2$], 90.8 (C-1), 89.7 (C=), 84.4 (C-4), 82.5 (C-2), 80.0 (C-3), 59.7, 59.6 ($2CH_2CH_3$), 55.3 (OCH_3), 54.3 (C-5), 26.0, 25.2 [$(CH_3)_2$C], 16.8 (C-6), 14.5, 14.4 ($2CH_2CH_3$); HREIMS m/z obsd 495.1936 calcd for $C_{24}H_{33}NO_8S$ 495.1927.

Acknowledgements

We thank the Dirección General de Enseñanza Superior e Investigación Científica of Spain and the Junta de Andalucia for financial support (grant numbers BQU2001-3740 and FQM-134), and the Ministerio de Educación Cultura y Deporte, and the Fundación Cámara of the University of Seville, for the award of fellowships to F.J.S., and J.M.I., respectively.

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