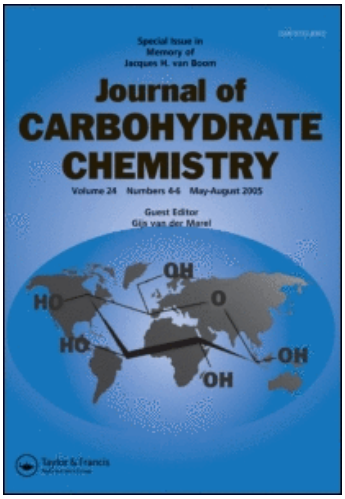

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Synthesis of Aza-Analogs of Natural and Artificial Desulfoglucosinolates

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SYNTHESIS OF AZA-ANALOGS OF NATURAL AND ARTIFICIAL DESULFOGLUCOSINOLATES[1]

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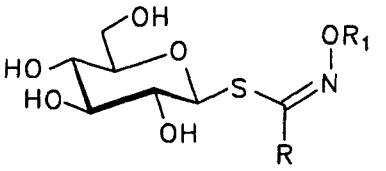
ABSTRACT

Addition of 2,3,4,6-tetra-*O*-acetyl-β-D-1-thio-glucopyranose (**3**) on selected nitrilimines, generated *in situ* from the corresponding hydrazonoyl halides **5**, gave the intermediate adducts **6** which were readily converted into glucosylthiohydrazonoates **7**, the *N*-phenyl aza-analogs of desulfoglucosinolates.

INTRODUCTION

Glucosinolates **1** constitute an important class of secondary plant compounds, which are mainly encountered in cruciferous vegetables. Glucosinolates include approximately 100 identified naturally occurring *O*-sulfated glucosylthiohydroximates, which only differ in the structure of the side-chain R.[2]



R= alkyl, alkenyl, aryl, hydroxyalkenyl, indol-3-ylmethyl

1 $R_1 = OSO_3K$

2 $R_1 = H$

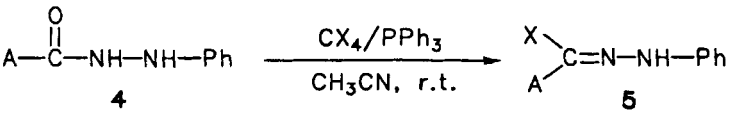
The enzyme myrosinase (thioglucoside glucohydrolase, EC 3.2.3.1) is also present in cruciferous plants and catalyzes the hydrolysis of glucosinolates **1**.[3] This reaction produces degradation compounds, e.g., isothiocyanates, thiocyanates and nitriles, which are in particular responsible for strong physiological activity in animals bred on rapeseed-based diets.[4]

Metabolism and nutritional studies of compounds **1** require the synthetic elaboration of structural analogs. In the course of our work on the synthesis and chemistry of non-natural glucosinolates and related structures,[5] we now report a general strategy for the preparation of aza-analogs of desulfated glucosinolates **2** through nucleophilic 1,3-addition of 2,3,4,6-tetra-*O*-acetyl-β-D-1-thio-glucopyranose (**3**) on selected nitrilimines,[6] generated *in situ* from the corresponding hydrazonoyl halides **5**, to afford 1-*S*-glucopyranosyl thiohydrazonoates (**6**). Standard *O*-deprotection of the sugar unit was then applied to convert the intermediates **6** into the target molecules **7**.

RESULTS AND DISCUSSION

N-phenylhydrazonoyl halides (**5a-h**) were prepared in fair to good yields (60-80%) by reaction of the corresponding hydrazides **4** with the triphenylphosphine-CCl_4 (or CBr_4) system in dry acetonitrile[7] (SCHEME I).

SCHEME I



compound	halide	A
5a	Cl	$-CH_3$
5b[8a]	Cl	$-CH_2-CH_3$
5c	Cl	$-CH_2-CH=CH_2$
5d	Cl	$-CH_2-CH_2-CH=CH_2$
5e[8b]	Br	-Ph
5f	Br	$-CH_2$-Ph
5g[8c]	Br	-CH=CH-Ph
5h	Br	indol-3-ylmethyl

Reaction of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**3**) on hydrazonoyl halides **5** in the presence of triethylamine led to the previously unknown 2,3,4,6-tetra-*O*-acetyl-1-*S*-(*N*-phenyl) alkyl- or arylhydrazonoyl-1-thio-β-D-glucopyranoses (**6a-h**) in 61-97% yield (SCHEME II). The formation in variable yields of the symmetrical β, β' - (2, 3, 4, 6 - tetra- *O* - acetyl - D - gluco pyranosyl) disulfide was the sole side-reaction observed by oxidative duplication of mercaptan **3**. The reaction time was *ca.* 1 h and *ca.* 4 h for hydrazonoyl bromides and chlorides respectively. ^{1}H NMR spectra data from the sugar moiety of compounds **6a-h** are reported in the TABLE.

The chemical shifts and coupling constants for the sugar ring protons are similar to those displayed by the thiosugar **3**, thus indicating that the $^4C_1$(D) conformation of the carbohydrate moiety remains unchanged regardless of the aglycon structure in the fully acetylated thiohydrazonoates **6**.

Glucosylthiohydrazonoates bearing a CH_2 "knuckle" (**6a-d, 6f, 6h**) proved rather unstable in chloroform solution. In those cases, the reverse reaction seems to occur affording a mixture of compounds, including 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**3**), the symmetrical β,β'-disulfide already mentioned and several unidentified nitrogen-containing degradation products.[9]

Finally, aza-analogs of desulfoglucosinolates **7** were obtained by *O*-deprotection of the sugar moiety using sodium methoxide in methanol (74-97%) (SCHEME II).

CONCLUSION

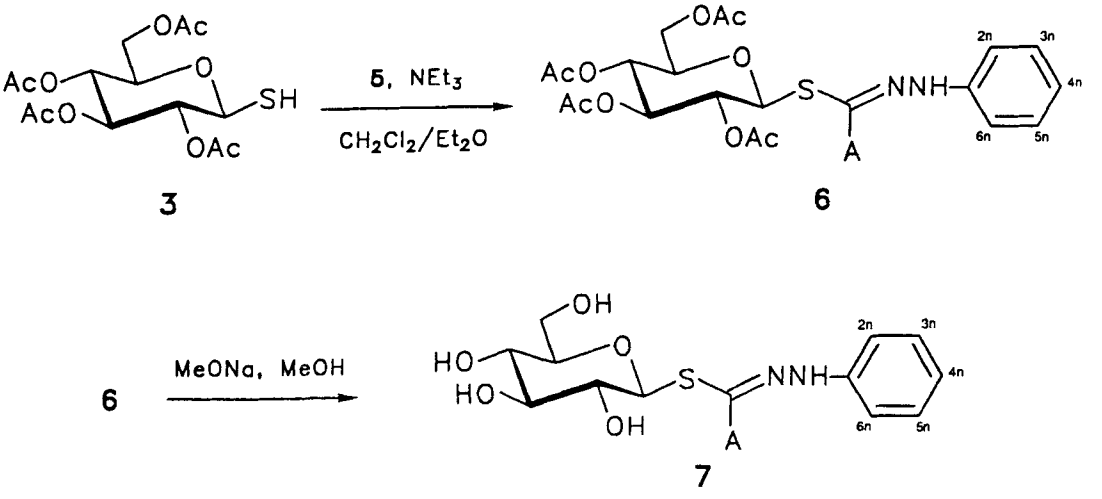
We have disclosed a general synthetic strategy to produce aza-analogs of desulfated glucosinolates. Metabolism and nutritional studies of compounds **7** are currently under way.

On the other hand, some of the intermediates **6** bearing an alkenyl side chain have further proven useful to develop intramolecular cyclization reactions which lead to new classes of thioglycosides.[10] Full results on that topic will be reported in due course.

EXPERIMENTAL

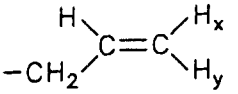
General procedure. Unless otherwise stated (compounds **6e** and **6f**) melting points were determined for crystalline samples (see ref. 9) on a Kofler-

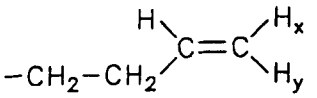
SCHEME II

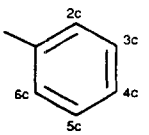


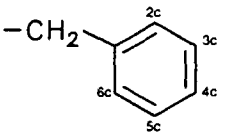
A= **a** $-CH_3$

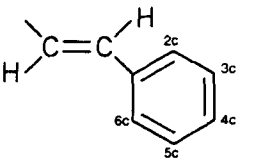
b $-CH_2-CH_3$

c 

d 

e 

f 

g 

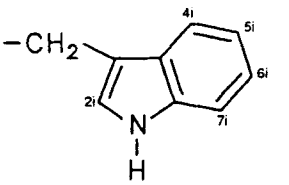
h 

TABLE. Proton chemical shifts and coupling constants of the sugar moiety in compounds **6a-h**.

Compd	H-1 $J_{1,2}$	H-2 $J_{2,3}$	H-3 $J_{3,4}$	H-4 $J_{4,5}$	H-5 $J_{5,6b}$	H-6a $J_{5,6a}$	H-6b $J_{6,6b}$	Acetyl
6a[a]	4.86d 9.7	5.07ft 9.7	5.23ft 9.7	5.09ft 9.7	3.73m 5.1	4.21dd 2.3	4.12dd 12.3	1.99s, 2.00s, 2.01s, 2.08s
6b[b]	4.76d 9.5	5.08ft 9.5	5.22ft 9.5	5.11ft 9.5	3.71m 5.2	4.21dd 2.4	4.12dd 12.3	1.97s, 2.00s, 2.01s, 2.08s
6c[b]	4.79d 9.7	5.08ft 9.7	5.21ft 9.7	5.13ft 9.7	3.69m 5.2	4.19dd 2.7	4.10dd 12.2	1.95s, 2.00s, 2.01s, 2.08s
6d[b]	4.75d 9.6	5.03ft 9.6	5.21ft 9.6	5.12ft 9.6	3.70m 5.1	4.19dd 2.2	4.11dd 12.2	1.96s, 2.01s, 2.02s,2.08s
6e[b]	4.65d 9.7	---------- 5.03-5.15m ---------- /	/	/	3.59m 5.1	4.17dd 2.1	4.04dd 12.4	1.89s, 1.99(2s), 2.04s
6f[b]	4.48d 9.5	4.97ft 9.5	---- 4.90-5.07m ---- /	/	3.46m 5.1	4.15dd 2.4	4.00dd 12.2	1.93s, 1.98s, 1.99s, 2.00s
6g[b]	4.69d 9.9	5.10ft 9.6	5.18ft 9.6	5.08ft 9.6	3.66m 5.3	4.19dd 2.1	4.05dd 12.3	1.82s, 1.99(2s), 2.08s
6h[b]	4.37d 9.5	---------- 4.90-5.00m ---------- /	/	/	3.10m 5.1	4.04dd 2.2	3.85dd 12.2	1.91s, 1.96(2s), 1.98s

a. In $(CD_3)_2CO$ at 27 °C.
b. In $CDCl_3$ at 27 °C.

block apparatus and are uncorrected. Optical rotations were measured with a Jobin Yvon type 71 polarimeter at 22 °C. IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded at 300 K in $CDCl_3$ (unless otherwise specified) for acetylated compounds and in DMSO-d_6 + D_2O for deprotected compounds on a Bruker AM-300 spectrometer (300.13 MHz). Chemical shifts are expressed in parts per million from TMS. Mass spectra were recorded on a NERMAG R-10-10-C spectrometer. Thin layer chromatography (TLC) was run on aluminium plates precoated with silica gel $60F_{254}$ (E. Merck, Darmstadt, Germany); detection was effected by observation under short wavelength UV light, or by dipping the chromatograms into a solution of ceric ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$] in 20% sulfuric acid and heating. Column chromatography was carried out with silica gel 60 (0.063-0.2 mm, E. Merck) and flash chromatogaphy was conducted with silica gel 60 (0.040-0.063 mm, E. Merck).

General preparation of hydrazonoyl halides (5a-h). To a solution of the hydrazide **4** (1 mmol) and triphenylphosphine (1.2 mmol) in dry acetonitrile (10 mL) was added the dry carbon tetrahalide (1 mmol CBr_4 or 3 mmol CCl_4). The mixture was stirred overnight at room temperature, then the solvent was concentrated *in vacuo*. The residue was chromatographed on a silica gel column using petroleum ether-ethyl acetate (7:3 v/v) as the eluent to give **5a-h**.

***N*-Phenyl Ethanhydrazonoyl Chloride** (**5a**, 146 mg, 87%); mp 48 °C; IR (KBr) 3310 (NH), 1580 (C=N), 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 1H, CH_3), 6.88 (t, 1H, J = 7.0 Hz, H-4n), 7.04 (d, 2H, J = 7.8 Hz, H-2n, H-6n), 7.27 (t, 2H, J = 7.4 Hz, H-3n, H-5n), 7.55 (bs, 1H, NH); LRMS (EI): m/z 170 $(M+2)^+$, 168 (M^+).

***N*-Phenyl Propanhydrazonoyl Chloride** (**5b**, 151 mg, 83%, oil[8a]); IR (neat) 3310 (NH), 1590 (C=N), 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3H, J = 7.1 Hz, $CH_2\mathbf{CH_3}$), 2.65 (q, 2H, J = 7.1 Hz, $\mathbf{CH_2}CH_3$), 6.87 (t, 1H, J = 7.1 Hz, H-4n), 7.03 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.25 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 7.60 (bs, 1H, NH); LRMS (EI): m/z 184 $(M+2)^+$, 182 (M^+).

***N*-Phenyl But-3-enhydrazonoyl Chloride** (**5c**, 161 mg, 83%, oil); IR (neat) 3310 (NH), 1600 (C=N), 750 and 690 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.37 (bd, 2H, J = 6.7 Hz, $\mathbf{CH_2}CH=CH_2$), 5.20-5.30 (m, 2H, $CH_2CH=\mathbf{CH_2}$), 5.80-6.00 (m, 1H, $CH_2\mathbf{CH}=CH_2$), 6.89 (t, 1H, J = 7.1 Hz, H-4n), 7.04 (d, 2H, J = 7.8 Hz, H-2n, H-6n), 7.25 (t, 2H, J = 7.4 Hz, H-3n, H-5n), 7.63 (bs, 1H, NH). LRMS (EI): m/z 196 $(M+2)^+$, 194 (M^+).

***N*-Phenyl Pent-4-enhydrazonoyl Chloride** (**5d**, 162 mg, 78%, oil); IR (neat) 3310 (NH), 1600 (C=N), 750 and 690 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5 (m, 2H, $CH_2\mathbf{CH_2}CH{=}CH_2$), 2.73 (t, 1H, J = 7.1 Hz, $\mathbf{CH_2}CH_2CH{=}CH_2$), 5.05 (bd, 1H, J = 10,2 Hz, Hx), 5.13 (dm, 1H, J = 17.4 Hz, Hy), 5.88 (m, 1H, $CH_2CH_2\mathbf{CH}{=}CH_2$), 6.90 (t, 1H, J = 7.6 Hz, H-4n), 7.05 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.27 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 7.63 (bs, 1H, NH). LRMS (EI): m/z 210 $(M+2)^+$, 208 (M^+).

***N*-Phenyl Benzhydrazonoyl Bromide** (**5e**, 165 mg, 60%); mp 110-113 °C (lit.[8b] mp 109-111 °C); IR (KBr) 3280 (NH), 750 and 690 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (t, 1H, J = 7.1 Hz, H-4n), 7.18 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.24-7.43 (m, 5H, H-3n, H-5n, H-4c, H-3c, H-5c), 7.90 (bd, 2H, J = 7.9 Hz, H-2c, H-6c), 8.03 (bs, 1H, NH). LRMS (EI): m/z 277 $(M+2)^+$, 275 (M^+).

***N*-Phenyl Phenylethanhydrazonoyl Bromide** (**5f**, 219 mg, 76%, oil); IR (neat) 3300 (NH), 1590 (C=N), 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.04 (s, 2H, $\mathbf{CH_2}Ph$), 6.91 (t, 1H, J = 7.1 Hz, H-4n), 7.06 (d, 2H, J = 8.0 Hz, H-2n, H-6n), 7.22-7.37 (m, 7H, H-3n, H-5n, H-2c, H-3c, H-4c, H-5c, H-6c), 7.64 (bs, 1H, NH). LRMS (EI): m/z 291 $(M+2)^+$, 289 (M^+).

***N*-Phenyl *(E)*-Cinnamhydrazonoyl Bromide** (**5g**, 211 mg, 70%); mp 149°C (lit.[8c] mp 153 °C); IR (KBr) 3290 (NH), 1600 (C=N), 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.94 (t, 1H, J = 7.3 Hz, H-4n), 6.98 (d, 1H, J = 15.3 Hz, $\mathbf{CH}{=}CHPh$), 7.11 (d, 1H, J = 15.3 Hz, $CH{=}\mathbf{CH}Ph$), 7.13 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.25-7.39 (m, 5H, H-3n, H-5n, H-3c, H-4c, H-5c), 7.49 (d , 2H, J = 7.5 Hz, H-2c, H-6c), 8.06 (bs, 1H, NH). LRMS (EI): m/z 303 $(M+2)^+$, 301 (M^+).

***N*-Phenyl Indol-3-ylethanhydrazonoyl Bromide** (**5h**, 197 mg, 60%, amorphous); IR (KBr) 3400 and 3300 (NH), 1600 (C=N), 750 and 690 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20 (s, 2H, CH_2), 6.90 (t, 1H, J = 7.1 Hz, H-4n); 7.07 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.11 (t, 1H, J = 7.5, H-5i), 7.18 (d, 1H, J = 2.0, H-2i), 7.20 (t, 1H, J = 7.5, H-6i), 7.27 (t, 2H, J = 7.5, H-3n, H-5n), 7.37 (d, 1H, J = 7.9, H-7i), 7.60 (s, 1H, NH), 7.68 (d, 1H, J = 7.9, H-4i), 8.06 (s, 1H, NH). LRMS (CI, NH_3): m/z 331 $(M+3)^+$, 229 $(M+1)^+$.

General procedure for the preparation of thiohydrazonoates (6a-h). A solution of triethylamine (0.42 mL, 3 mmol) in methylene chloride (5mL) was added dropwise to a solution of 2,3,4,6 tetra-*O*-acetyl-β-D-1-thio-glucopyranose (**3**) (364 mg, 1 mmol) and the hydrazonoyl halide **5** (1.2 mmol) in methylene chloride-diethyl ether (10 mL 1:2 v/v) under nitrogen. The resulting solution was kept at room temperature for 4 h or 1 h (t) until completion of the reaction

(TLC). The reaction mixture was washed with a 0.5 M sulfuric acid solution. The organic layer collected was then dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography with petroleum ether-ethyl acetate (7:3 v/v) as the eluent to give crystalline **6a-h**.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Ethanhydrazonoyl)-1-thio-β-D-glucopyranose (**6a**, 300 mg, 61%, t 4 h); mp 121 °C; $[\alpha]_D$ +6° (*c* 1,0, acetone); IR (KBr) 3300 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 2.35 (s, 3H, CH_3), 6.86 (t, 1H, J = 7.2 Hz, H-4n), 7.03 (d, 1H, J = 7.7 Hz, H-2n, H-6n), 7.23 (t, 1H, J = 7.7 Hz, H-3n, H-5n). LRMS (CI, NH_3): m/z 497 $(M+1)^+$. HRMS Calcd for $C_{22}H_{28}N_2O_9S$: 496.1515. Found: 496.1497.

2, 3, 4, 6 -Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Propanhydrazonoyl)-1-thio-β-D-glucopyranose (**6b**, 393 mg, 77%, t 4 h); mp 136 °C; $[\alpha]_D$ +48° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1050, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 1.25 (t, 3H, J = 7.0 Hz, $CH_2\mathbf{CH_3}$), 2.60 (q, 2H, J = 7.0 Hz, $\mathbf{CH_2}CH_3$), 6.87 (t, 1H, J = 7.3 Hz, H-4n), 7.04 (d, 1H, J = 8.0 Hz, H-2n, H-6n), 7.25 (t, 1H, J = 7.5 Hz, H-3n, H-5n); LRMS (CI, NH_3): m/z 511 $(M+1)^+$. HRMS Calcd for $C_{23}H_{30}N_2O_9S$: 510.1672. Found: 510.1666.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl But-3-enhydrazonoyl)-1-thio-β-D-glucopyranose (**6c**, 407 mg, 78%, t 4 h); mp 115 °C; $[\alpha]_D$ +44° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1590 (C=N), 1210 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 3.35 (bd, 2H, J = 6.6 Hz, $\mathbf{CH_2}CH=CH_2$), 5.18 (m, 2H, $CH_2CH=\mathbf{CH_2}$), 6.04-5.90 (m, 1H, $CH_2\mathbf{CH}=CH_2$), 6.87 (t, 1H, J = 7.3 Hz, H-4n), 7.05 (d, 1H, J = 8.2 Hz, H-2n, H-6n), 7.24 (t, 1H, J = 7.6 Hz, H-3n, H-5n). LRMS (CI, NH_3): m/z 523 $(M+1)^+$. HRMS Calcd for $C_{24}H_{30}N_2O_9S$: 522.1672. Found: 522.1658.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Pent-4-enhydrazonoyl)-1-thio-β-D-glucopyranose (**6d**, 407 mg, 76%, t 4 h); mp 90 °C; $[\alpha]_D$ +46° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 2.46 (q, 2H, J = 6.7 Hz, $\mathbf{CH_2}CH_2CH=CH_2$), 2.67 (t, 2H, J = 6.7 Hz, $CH_2\mathbf{CH_2}CH=CH_2$), 5.03 (m, 2H, $CH_2CH_2CH=\mathbf{CH_2}$), 5.87 (m, 1H, $CH_2CH_2\mathbf{CH}=CH_2$), 6.87 (t, 1H, J = 7.1 Hz, H-4n), 7.05 (d, 1H, J = 8.9 Hz, H-2n, H-6n), 7.24 (t, 1H, J = 7.6 Hz, H-3n, H-5n). LRMS (CI, NH_3): m/z 537 $(M+1)^+$. HRMS Calcd for $C_{25}H_{32}N_2O_9S$: 536.1828. Found: 536.1831.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Benzhydrazonoyl)-1-thio-β-D-glucopyranose (**6e**, 541 mg, 97%, t 1 h); mp 149 °C (ethanol); $[\alpha]_D$ +149° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 6.93 (t, 1H, J = 7.2 Hz, H-4n), 7.20 (d, 2H, J = 8.2 Hz, H-2n, H-6n), 7.27-7.41 (m, 6H, H-3n, H-5n, H-3c, H-4c, H-5c), 7.94 (d, 2H, J = 7.7 Hz, H-2c, H-6c). LRMS (CI, NH_3): m/z 559 $(M+1)^+$. HRMS Calcd for $C_{27}H_{30}N_2O_9S$: 558.1672. Found: 558.1651.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Phenylethanhydrazonoyl)-1-thio-β-D-glucopyranose (**6f**, 458 mg, 80%, t 1 h); mp 123 °C (ethanol); $[\alpha]_D$ +55° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 3.86 and 3.97 (2d, 2H, J_{gem} = 15.0 Hz, **CH_2**Ph), 6.88 (t, 1H, J = 7.3 Hz, H-4n), 7.06 (d, 2H, J = 8.2 Hz, H-2n, H-6n), 7.23-7.33 (m, 7H, H-3n, H-5n, H-2c, H-3c, H-4c, H-5c, H-6c), 8.50 (bs, 1H, NH). LRMS (CI, NH_3): m/z 573 $(M+1)^+$. HRMS Calcd for $C_{28}H_{32}N_2O_9S$: 572.1828. Found: 572.1811.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl *(E)*-Cinnamhydrazonoyl)-1-thio-β-D-glucopyranose (**6g**, 555 mg, 95%, t 1 h); mp 164 °C; $[\alpha]_D$ +141° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 6.88 (t, 1H, J = 7.3 Hz, H-4n), 7.08 (d, 1H, J = 15.8 Hz, **CH**=CHPh), 7.13 (d, 2H, J = 8.2 Hz, H-2n, H-6n), 7.14 (d, 1H, J = 15.8 Hz, CH=**CH**Ph), 7.26-7.37 (m, 5H, H-3n, H-5n, H-3c, H-4c, H-5c), 7.45 (d, 2H, J= 7.7 Hz, H-2c, H-6c). LRMS (CI, NH_3): m/z 585 $(M+1)^+$. HRMS Calcd for $C_{29}H_{32}N_2O_9S$: 584.1828. Found: 584.1820.

2, 3, 4, 6 - Tetra - *O* - acetyl-1-*S*-(*N*-phenyl Indol-3-ylethanhydrazonoyl)-1-thio-β-D-glucopyranose (**6h**, 459 mg, 75%, t 1 h, amorphous); $[\alpha]_D$ +24° (*c* 1.0, acetone); IR (KBr) 3280 (NH), 1740 (C=O), 1600 (C=N), 1230 (C-S and C-O-C), 1040, 750 and 700 (C=C aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) TABLE and δ 4.00 and 4.12 (2d, 2H, J_{gem}= 15.8 Hz, CH_2), 6.86 (t, 1H, J= 7.1 Hz, H-4n), 7.08 (t, 1H, J = 7.9 Hz, H-5i), 7.09 (d, 2H, J= 7.9 Hz, H-2n, H-6n), 7.12 (d, 1H, J = 2.0 Hz, H-2i), 7.19 (t, 1H, J= 7.9 Hz, H-6i), 7.26 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 7.38 (d, 1H , J = 7.9 Hz, H-7i), 7.68 (d, 1H, J = 7.9 Hz, H-4i), 8.06 (bs, 1H, NH), 8.50 (bs, 1H, NH). LRMS (CI, NH_3): m/z 613 $(M+1)^+$. HRMS Calcd for $C_{30}H_{33}N_3O_9S$: 611.1937. Found: 611.1941.

General procedure for the preparation of aza-analogs of desulfoglucosinolates (7a-h). To a stirred solution of **6** (1 mmol) in methanol (10mL) was added 5 drops of a freshly prepared 1M solution of sodium methoxide in

methanol. The mixture was stirred at room temperature while the course of the reaction was monitored by TLC. The solution was neutralized by DOWEX 50 W ion-exchange resin (acid form), filtered and concentrated. The residue obtained was chromatographed on a silica gel column using methylene chloride-methanol (9:1 v/v) as the eluent to yield compounds **7** as amorphous solids.

1-*S*-(*N*-Phenyl Ethanhydrazonoyl)-1-thio-β-D-glucopyranose (7a, 243 mg, 74%); $[\alpha]_D$ -30° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 2.30 (s, 3H, CH_3), 3.03-3.27 (m, 4H, H-2, H-3, H-4, H-5), 3.38 (dd, 1H, $J_{5,6b}$ = 5.9, H-6b), 3.67 (bd, 1H, $J_{6a,6b}$ = 11.8, H-6a), 4.82 (d, 1H, $J_{1,2}$ = 9.6, H-1), 6.71 (t, 1H, J = 7.1 Hz, H-4n), 7.02 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.14 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 8.50 (s, 1H, NH). LRMS (CI, NH_3): m/z 329 $(M+1)^+$. HRMS Calcd for $C_{14}H_{20}N_2O_5S$: 328.1093. Found: 328.1105.

1-*S*-(*N*-Phenyl Propanhydrazonoyl)-1-thio-β-D-glucopyranose (7b, 274 mg, 80%); $[\alpha]_D$ -44° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 1.17 (t, 3H, J = 7.0 Hz, $CH_2\mathbf{CH_3}$), 2.61 (q, 2H, J = 7.0 Hz, $\mathbf{CH_2}CH_3$), 2.98-3.25 (m, 4H, H-2, H-3, H-4, H-5), 3.42 (dd, 1H, $J_{5,6b}$ = 5.7, H-6b), 3.67 (bd, 1H, $J_{6a,6b}$ = 11.7, H-6a), 4.67 (d, 1H, $J_{1,2}$ = 9.5, H-1), 6.72 (t, 1H, J = 7.3 Hz, H-4n), 7.07 (d, 2H, J = 8.2 Hz, H-2n, H-6n), 7.16 (t, 2H, J = 7.8 Hz, H-3n, H-5n), 8.84 (s, 1H, NH). LRMS (CI, NH_3): m/z 343 $(M+1)^+$. HRMS Calcd for $C_{15}H_{22}N_2O_5S$: 342.1249. Found: 342.1239.

1-*S*-(*N*-Phenyl But-3-enhydrazonoyl)-1-thio-β-D-glucopyranose (7c, 251 mg, 71%); $[\alpha]_D$ -36° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 3.03-3.25 (m, 4H, H-2, H-3, H-4, H-5), 3.38 (m, 2H, $\mathbf{CH_2}CH{=}CH_2$), 3.41 (dd, 1H, $J_{5,6b}$ = 5.8, H-6b), 3.69 (bd, 1H, $J_{6a,6b}$ = 11.8, H-6a), 4.73 (d, 1H, $J_{1,2}$ = 9.7, H-1), 5.10 (bd, 1H, J = 10.3 Hz, Hx), 5.16 (bd, 1H, J = 17.2 Hz, Hy), 5.95-6.09 (m, 1H, $CH_2\mathbf{CH}{=}CH_2$), 6.73 (t, 1H, J = 7.2 Hz, H-4n), 7.06 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.16 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 8.86 (s, 1H, NH). LRMS (CI, NH_3): m/z 355 $(M+1)^+$. HRMS Calcd for $C_{16}H_{22}N_2O_5S$: 354.1249. Found: 354.1228.

1-*S*-(-*N*-Phenyl Pent-4-enhydrazonoyl)-1-thio-β-D-glucopyranose (7d, 295 mg, 75%); $[\alpha]_D$ -40° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 2.42 (m, 2H, $\mathbf{CH_2}CH_2CH{=}CH_2$), 2.66 (m, 2H, $CH_2\mathbf{CH_2}CH{=}CH_2$), 3.02-3.35 (m, 4H, H-2, H-3, H-4, H-5), 3.43 (dd, 1H, $J_{5,6b}$ = 5.7, H-6b), 3.67 (bd, 1H, $J_{6a,6b}$ = 11.8, H-6a), 4.64 (d, 1H, $J_{1,2}$ = 10.0, H-1), 4.97 (bd, 1H, J = 10.6 Hz, Hx), 5.09 (bd, 1H, J = 17.2 Hz, Hy), 5.80-5.95 (m, 1H, $CH_2CH_2\mathbf{CH}{=}CH_2$), 6.73 (t, 1H, J = 7.2 Hz, H-4n), 7.06 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.16 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 8.92 (s, 1H, NH). LRMS (CI, NH_3): m/z 369 $(M+1)^+$. HRMS Calcd for $C_{17}H_{24}N_2O_5S$: 368.1406. Found: 368.1396.

1-*S*-(*N*-Phenyl Benzhydrazonoyl)-1-thio-β-D-glucopyranose (**7e**, 312 mg, 80%); $[\alpha]_D$ -19° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 3.03-3.15 (m, 4H, H-2, H-3, H-4, H-5), 3.42 (dd, 1H, $J_{5,6b}$ = 5.1, H-6b), 3.60 (bd, 1H, $J_{6a,6b}$ = 11.4, H-6a), 4.36 (d, 1H, $J_{1,2}$ = 9.5, H-1), 6.85 (t, 1H, J = 7.1 Hz, H-4n), 7.17-7.42 (m, 7H, H-2n, H-3n, H-5n, H-6n, H-3c, H-4c, H-5c), 7.96 (d, 2H, J = 7.7 Hz, H-2c, H-6c), 9.94 (s, 1H, NH). LRMS (CI, NH_3): m/z 391 $(M+1)^+$. HRMS Calcd for $C_{19}H_{22}N_2O_5S$: 390.1249. Found: 390.1252.

1-*S*-(*N*-Phenyl Phenylethanhydrazonoyl)-1-thio-β-D-glucopyranose (**7f**, 364 mg, 90%); $[\alpha]_D$ -36° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 3.00-3.20 (m, 4H, H-2, H-3, H-4, H-5), 3.42 (dd, 1H, $J_{5,6b}$ = 5.5, H-6b), 3.69 (bd, 1H, $J_{6a,6b}$ = 11.6, H-6a), 3.88 and 3.96 (d, 2H, J = 15.0 Hz, CH_2Ph), 4.54 (d, 1H, $J_{1,2}$ = 9.5, H-1), 6.74 (t, 1H, J = 7.1 Hz, H-4n), 7.02 (d, 2H, J = 7.9 Hz, H-2n, H-6n), 7.16 (t, 2H, J = 7.5 Hz, H-3n, H-5n), 7.20-7.38 (m, 5H, H-2c, H-3c, H-4c, H-5c, H-6c), 8.98 (s, 1H, NH). LRMS (CI, NH_3): m/z 405 $(M+1)^+$. HRMS Calcd for $C_{20}H_{24}N_2O_5S$: 404.1406. Found: 404.1392.

1-*S*-(*N*-Phenyl (*E*)-Cinnamhydrazonoyl)-1-thio-β-D-glucopyranose (**7g**, 375 mg, 90%); $[\alpha]_D$ +11° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 3.05-3.21 (m, 4H, H-2, H-3, H-4, H-5), 3.45 (dd, 1H, $J_{5,6b}$ = 5.4, H-6b), 3.66 (bd, 1H, $J_{6a,6b}$ = 11.4, H-6a), 4.41 (d, 1H, $J_{1,2}$ = 9.5, H-1), 6.86 (t, 1H, J = 7.1 Hz, H-4n), 7.08-7.39 (m, 9H, CH=CHPh, H-2n, H-3n, H-5n, H-6n, H-3c, H-4c, H-5c), 7.56 (d, 2H, J = 7.9 Hz, H-2c, H-6c), 9.98 (s, 1H, NH). LRMS (CI, NH_3): m/z 417 $(M+1)^+$. HRMS Calcd for $C_{21}H_{24}N_2O_5S$: 416.1406. Found: 416.1404.

1-*S*-(*N*-Phenyl Indol-3-ylethanhydrazonoyl)-1-thio-β-D-glucopyranose (**7h**, 358 mg, 80%); $[\alpha]_D$ -26° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6+D_2O) δ 3.01-3.20 (m, 4H, H-2, H-3, H-4, H-5), 3.45 (dd, 1H, $J_{5,6b}$ = 5.5, H-6b), 3.70 (bd, 1H, $J_{6a,6b}$ = 11.8, H-6a), 3.96 and 4.10 (d, 2H, J = 15.4 Hz, CH_2), 4.65 (d, 1H, $J_{1,2}$ = 9.5, H-1), 6.74 (t, 1H, J = 7.1 Hz, H-4n), 6.93 (t, 1H, J = 7.7 Hz, H-6i), 7.04 (t, 1H, J = 7.7 Hz, H-5i), 7.09 (d, 2H, J = 8.3 Hz, H-2n, H-6n), 7.17 (t, 2H, J = 7.3 Hz, H-3n, H-5n), 7.24 (d, 1H, J = 2.0 Hz, H-2i), 7.33 (d, 1H, J = 7.7 Hz, H-7i), 7.59 (d, 1H, J = 7.7 Hz, H-4i). LRMS (CI, NH_3): m/z 444 $(M+1)^+$. HRMS Calcd for $C_{22}H_{25}N_3O_5S$: 443.1515. Found: 443.1506.

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