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(Z)-STEREOSPECIFIC ADDITION OF GLYCOSYLMERCAPTANS ON NITRILIUM BETAINES.[1] SYNTHESIS OF 1-*S*-GLUCOPYRANOSYL ARYLTHIOHYDROXIMATES

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Abstract: With a view to selecting new internal standards for HPLC analysis of glucosinolates, the synthesis of artificial desulfoglucosinolates **5** was carried out.

Glucosinolates **1** constitute a structurally homogeneous class of naturally-occurring sulfated (*Z*)-glucosylthiohydroximates which are present in *Cruciferae* and particularly in the economically important crop, oil-seed rape.[2]

The antinutritional character of compounds **1** in animal diets entails the need for accurate analytical determination of the composition and the amounts present in the seeds and the meal produced therefrom. The only two commercially available natural glucosinolates - sinigrin (A= vinyl) and glucotropaeolin (A= phenyl) - are far from being fully satisfactory for internal standardization of the chromatographic analyses.

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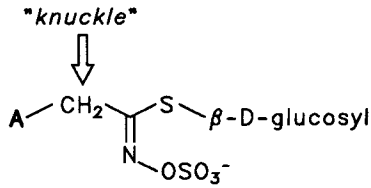


1

A= alkyl, alkenyl, hydroxyalkenyl, aryl, indol-3-yl, methylthio(or-sulfinyl or-sulfonyl)alkyl

Therefore, we planned to synthesize a broad range of totally artificial (devoid of the CH_2 "knuckle") desulfoglucosinolate analogues **5** with a view to selecting several new customized standards for the HPLC analysis of natural glucosinolates.

The key step for the synthesis of compounds **5** (scheme 1) consisted in the nucleophilic 1,3-addition of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**3**)[3] on transient nitrile oxides ACN^+-O^-, produced *in situ* by the action of triethylamine upon the corresponding hydroximoyl chlorides **2**.

These "chloro-oximes" **2** can be routinely prepared by standard chlorination of the corresponding aldoximes using either chlorine gas[4] or N-chlorosuccinimide (NCS).[5]

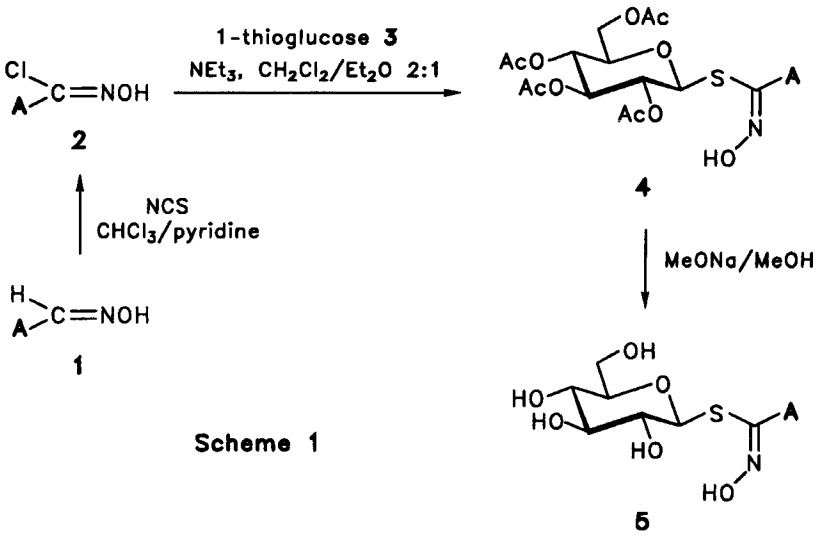
In the first case however, it has been observed that Cl_2 can induce side reactions by substituting phenyl moieties which bear electron-donating groups.[6] To circumvent this problem, NCS was uniformly used as the chlorinating agent.

1-*S*-Glucopyranosyl arylthiohydroximates **4a-l** were thus obtained in fair to excellent yields (65-93%) and with a complete stereocontrol (*Z* configuration of the hydroxyimino moiety). In contrast with the preceding general method, the *p*-amino derivative **4m** was prepared from **4d** in 72% yield (scheme 2) by tin(II) chloride reduction of the nitro group.

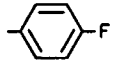
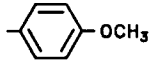
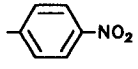
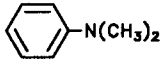
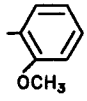
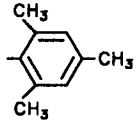
Characterization data and ^1H NMR data for the thiohydroximate derivatives **4a-m** are reported in Tables 1 and 2, respectively.

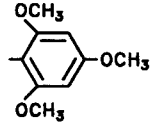
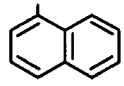
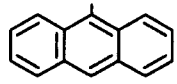
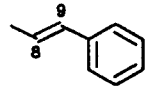
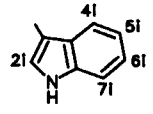
Quantitative deprotection of the sugar unit readily converted the intermediate compounds **4** into the desired non-sulfated artificial glucosinolates **5** suitable for chromatogram standardization. Physical properties and spectroscopic data for compounds **5a-m** are reported in Tables 3 and 4.

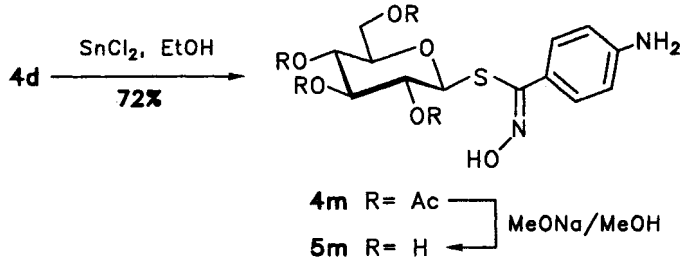
Analytical evaluation of the standard candidates is currently under investigation.[7]



Scheme 1

1,2,4,5	A
a	
b	
c	
d	
e	
f	
g	

1,2,4,5	A
h	
i	
j	
k	
l	



Scheme 2

EXPERIMENTAL

Melting points were determined with a Kofler-block apparatus and are uncorrected. Optical rotations were measured with a Jobin-Yvon Digital type 71 polarimeter at 22°C. NMR spectra were recorded at 300°K in $CDCl_3$ (unless otherwise specified) on a Bruker AM 300 (300.13 MHz for ^1H). Chemical shifts are expressed in parts per million downfield from TMS. Mass spectra were recorded on Nermag-R-10-10C (LRMS). Thin layer chromatography 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 (254 nm), then by dipping the chromatograms into a solution of ceric ammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$ in 20% sulfuric acid and charring them with a heat gun. Column chromatography was performed using silica gel 60 (0.063-0.200 mm, E. Merck).

General procedure for the synthesis of hydroximoyl chlorides 2a-l. Oxime **1** (7.5 mmol) was dissolved in a flask containing chloroform (15 mL) and pyridine (0.3 mL). N-chlorosuccinimide (7.5 mmol) was slowly added at 0°C, then the reaction mixture was stirred 2 h at room temperature. After washing, the organic layer was dried over anhydrous magnesium sulfate and concentrated, giving product **2** which was used directly in the next step without further purification.

General procedure for the synthesis of (Z)-1-S-glucopyranosyl arylthiohydroximates 4a-l. To a stirred solution of the hydroximoyl chloride **2** (1.2 mmol) in an Et_2O/CH_2Cl_2 mixture (15 mL 2:1 v/v) under argon, **3** (1 mmol) dissolved in CH_2Cl_2 (5mL) and NEt_3 (3 mmol) were successively added. Triethylammonium hydrochloride immediately precipitated from the solution.

Table 1: Yields and data for compounds **4**

Product	Yield (%)	mp (°C)	$[\alpha]_D$ (*c* 1.0, $CHCl_3$)	Molecular Formula[a]	MS (CI, NH_3)
4a[6]	90	118	+19°	$C_{21}H_{25}NO_{10}S$ (483.48)	484 $(M+1)^+$
4b	65	143	+39°	$C_{21}H_{24}FNO_{10}S$ (501.47)	502 $(M+1)^+$
4c	71	150	+13°	$C_{22}H_{27}NO_{11}S$ (513.51)	514 $(M+1)^+$
4d	60	amorphous	+8°	$C_{21}H_{24}N_2O_{12}S$ (528.48)	529 $(M+1)^+$
4e	85	133	+17°	$C_{23}H_{30}N_2O_{10}S$ (526.55)	527 $(M+1)^+$
4f	56	oil	-6°	$C_{22}H_{27}NO_{11}S$ (513.51)	514 $(M+1)^+$
4g	80	177	+38°	$C_{24}H_{31}NO_{10}S$ (525.56)	526 $(M+1)^+$
4h	94	amorphous	+27°	$C_{24}H_{31}NO_{13}S$ (573.56)	574 $(M+1)^+$
4i	95	amorphous	+29°	$C_{25}H_{27}NO_{10}S$ (533.54)	534 $(M+1)^+$
4j	96	amorphous	-11°	$C_{25}H_{27}NO_{10}S$ (583.59)	584 $(M+1)^+$
4k	91	190	-74°	$C_{23}H_{27}NO_{10}S$ (509.52)	510 $(M+1)^+$
4l	93	amorphous	+14°	$C_{23}H_{26}N_2O_{10}S$ (522.52)	523 $(M+1)^+$
4m	72 (from **4d**)	amorphous	+12°	$C_{21}H_{26}N_2O_{10}S$ (498.49)	499 $(M+1)^+$

[a]Satisfactory microanalysis obtained for compounds **4**: C±0.25 H±0.25 N±0.22.

Table 2: ^{1}H NMR data for compounds **4**.

Compd.	^{1}H NMR ($CDCl_3$) δ (ppm), *J* (Hz)
4a	1.96, 1.97, 2.06, 2.10 (4s, 12H, OAc), 3.04 (m, 1H, H-5), 3.95 (dd, 1H, $J_{5,6b}$= 2.2, H-6b), 4.09 (dd, 1H, $J_{5,6a}$= 5.0, $J_{6a,6b}$= 12.2, H-6a), 4.46 (d, 1H, $J_{1,2}$= 9.9, H-1), 4.94-5.12 (m, 3H, H-2, H-3, H-4), 7.40-7.50 (m, 3H, H_{Ar}), 7.52-7.57 (m, 2H, H_{Ar}).
4b	1.97, 2.06, 2.12 (3s, 12H, OAc), 3.14 (m, 1H, H-5), 3.98 (dd, 1H, $J_{5,6b}$= 2.4, H-6b), 4.12 (dd, 1H, $J_{5,6a}$= 4.7, $J_{6a,6b}$= 11.8, H-6a), 4.50 (d, 1H, $J_{1,2}$= 9.9, H-1), 4.94-5.08 (m, 3H, H-2, H-3, H-4), 7.13 (ft, 2H, $J_{orthoH,H}$= 8.5, $J_{orthoH,F}$= 8.5, H_{Ar}), 7.55 (dd, 2H, $J_{metaH,F}$= 5.3, H_{Ar}).
4c	1.98, 2.07, 2.09 (3s, 12H, OAc), 3.15 (m, 1H, ,H-5), 3.86 (s, 3H, CH_3), 4.00 (dd, 1H, $J_{5,6b}$= 2.3, H-6b), 4.14 (dd, 1H, $J_{5,6a}$= 4.5, $J_{6a,6b}$= 12.0, H-6a), 4.50 (d, 1H, $J_{1,2}$= 9.0, H-1), 5.01-5.12 (m, 3H, H-2, H-3, H-4), 6.94 (d, 2H, J= 8.8, H_{Ar}), 7.47 (d, 2H, J= 8.8, H_{Ar}).
4d	1.99, 2.07, 2.09 (3s, 12H, OAc), 3.25 (m, 1H, H-5), 4.01 (dd, 1H, $J_{5,6b}$= 2.4, H-6b), 4.13 (dd, 1H, $J_{5,6a}$= 5.4, $J_{6a,6b}$= 12.7,H-6a), 4.64 (d, 1H, $J_{1,2}$= 9.1, H-1), 4.98-5.09 (m, 3H, H-2, H-3, H-4), 7.85 (d, 2H, J= 7.9, H_{Ar}), 8.29 (d, 1H, J= 7.9, H_{Ar}).
4e	1.97, 1.98, 2.05, 2.10 (4s, 12H, OAc), 3.03 (s, 6H, CH_3), 3.22 (m, 1H, H-5), 4.02 (dd, 1H, $J_{5,6b}$= 2.2, H-6b), 4.16 (dd, 1H, $J_{5,6a}$= 4.7, $J_{6a,6b}$= 12.3, H-6a), 4.57 (d, 1H, $J_{1,2}$= 9.6, H-1), 5.00-5.14 (m, 3H, H-2, H-3, H-4), 6.69 (d, 2H, J= 8.8, H_{Ar}), 7.40 (d, 2H, J= 8.8, H_{Ar}).
4f	1.95, 1.97, 2.06, 2.10 (4s, 12H, OAc), 2.80 (m, 1H, H-5), 3.75 (dd, 1H, $J_{5,6b}$= 1.9, H-6b), 3.82 (s, 3H, CH_3), 4.03 (dd, 1H, $J_{5,6a}$= 4.1, $J_{6a,6b}$= 12.6, H-6a), 4.30 (d, 1H, $J_{1,2}$= 9.5, H-1), 4.95-5.12 (m, 3H, H-2, H-3, H-4), 6.97-7.03 (m, 2H, H_{Ar}), 7.30 (bd, 1H, J= 7.7, H_{Ar}), 7.44 (t, 1H, J= 7.7, H_{Ar}).

4g 1.94, 1.97, 2.05, 2.09 (4s, 12H, OAc), 2.25 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.75 (m, 1H, H-5), 3.90 (dd, 1H, $J_{5,6b}$= 2.4, H-6b), 3.96 (d, 1H, $J_{1,2}$= 9.5, H-1), 4.05 (dd, 1H, $J_{5,6a}$= 4.7, $J_{6a,6b}$= 11.8, H-6a), 4.93-5.05 (m, 3H, H-2, H-3, H-4), 6.91 (bs, 1H, H_{Ar}), 6.93 (bs, 1H, H_{Ar}).

4h 1.96, 1.98, 2.04 (3s, 12H, OAc), 2.87 (m, 1H, H-5), 3.77 (dd, 1H, $J_{5,6b}$= 2.5, H-6b), 3.81 (s, 6H, CH_3), 3.87 (s, 3H, CH_3), 4.07 (dd, 1H, $J_{5,6a}$= 2.8, $J_{6a,6b}$= 12.1, H-6a), 4.29 (d, 1H, $J_{1,2}$= 9.4, H-1), 4.98-5.10 (m, 3H, H-2, H-3, H-4), 6.13 (s, 2H, H_{Ar}).

4i 1.87, 1.93, 2.04, 2.06 (4s, 12H, OAc), 2.38 (m, 1H, H-5), 3.24 (d, 1H, H-6b), 3.82 (dd, 1H, $J_{5,6a}$= 3.6, $J_{6a,6b}$= 11.9, H-6a), 4.01 (d, 1H, $J_{1,2}$= 9.5, H-1), 4.76 (ft, 1H, $J_{3,4}$= 9.5, H-3), 4.90 (ft, 1H, $J_{4,5}$= 9.5, H-4), 5.00 (ft, 1H, $J_{2,3}$= 9.5, H-2), 7.50-7.60 (m, 4H, H_{Ar}), 7.78-8.08 (m, 3H, H_{Ar}).

4j 1.76, 1.86, 1.98, 2.00 (4s, 12H, OAc), 2.06 (m, 1H, H-5), 2.64 (dd, 1H, $J_{5,6b}$= 2.1, H-6b), 3.59 (dd, 1H, $J_{5,6a}$= 3.6, $J_{6a,6b}$= 12.3, H-6a), 3.59 (d, 1H, $J_{1,2}$= 10.2, H-1), 4.49 (ft, 1H, $J_{3,4}$= 9.5, H-3), 4.80 (ft, 1H, $J_{4,5}$= 9.5, H-4), 4.92 (ft, 1H, $J_{2,3}$= 9.5, H-2), 7.48-7.57 (m, 4H, H_{Ar}), 7.99-8.17 (m, 4H, H_{Ar}), 8.58 (s, 1H, H_{Ar}).

4k 2.00, 2.03 2.08 (3s, 12H, OAc), 3.72 (m, 1H, H-5), 4.11 (dd, 1H, $J_{5,6b}$= 2.4, H-6b), 4.25 (dd, 1H, $J_{5,6a}$= 5.5, $J_{6a,6b}$= 11.8, H-6a), 5.05 (d, 1H, $J_{1,2}$= 9.5, H-1), 5.08-5.26 (m, 3H, H-2, H-3, H-4), 6.85 (d, 1H, $J_{8,9}$= 16.0, H-8), 7.27 (d, 1H, H-9), 7.34-7.52 (m, 5H, H_{Ar}).

4l 1.96, 2.00, 2.03, 2.05 (4s, 12H, OAc), 3.21 (m, 1H, H-5), 3.90 (dd, 1H, $J_{5,6b}$= 2.4, H-6b), 4.14 (dd, 1H, $J_{5,6a}$= 4.7, $J_{6a,6b}$= 12.3, H-6a), 4.91 (d, 1H, $J_{1,2}$= 9.5, H-1), 5.01-5.14 (m, 3H, H-2, H-3, H-4), 7.19 (ft, 1H, J= 7.2, H-5i), 7.26 (ft, 1H, J= 7.2,H-6i), 7.36 (d, 1H, J= 8.2, H-7i), 7.56 (d, 1H, $J_{2i,NH}$= 2.4, H-2i), 7.95 (d, 1H, J= 8.2, H-4i).

4m 1.97, 1.98, 2.05, 2.11 (4s, 12H, OAc), 3.20 (m, 1H, H-5), 3.92 (bs, 2H, NH_2), 4.00 (dd, 1H, $J_{5,6b}$= 2.3, H-6b), 4.14 (dd, 1H, $J_{5,6a}$= 4.9, $J_{6a,6b}$= 12.3, H-6a), 4.56 (d, 1H, $J_{1,2}$= 9.6, H-1), 4.98-5.13 (m, 3H, H-2, H-3, H-4), 6.69 (d, 2H, J= 8.7, H_{Ar}), 7.33 (d, 2H, J= 8.7, H_{Ar}).

Table 3: Yields and data for compounds **5**.

Product	Yield (%)	mp (°C)	$[\alpha]_D$ (*c* 1.0, MeOH)	Molecular Formula[a]	MS (CI, NH_3)
5a	94	oil	-2°	$C_{13}H_{17}NO_6S$ (315.34)	316 $(M+1)^+$
5b	95	104	+29°	$C_{13}H_{16}FNO_6S$ (333.33)	334 $(M+1)^+$
5c	97	amorphous	-7°	$C_{14}H_{19}NO_7S$ (345.36)	346 $(M+1)^+$
5d	91	amorphous	+5°	$C_{13}H_{16}N_2O_8S$ (360.34)	361 $(M+1)^+$
5e	98	138	+21°	$C_{15}H_{22}N_2O_6S$ (358.40)	359 $(M+1)^+$
5f	95	oil	-8°	$C_{14}H_{19}NO_7S$ (345.36)	346 $(M+1)^+$
5g	90	210	-23°	$C_{16}H_{23}NO_6S$ (357.41)	358 $(M+1)^+$
5h	98	amorphous	+4°	$C_{16}H_{23}NO_9S$ (405.42)	406 $(M+1)^+$
5i	89	amorphous	-1°	$C_{17}H_{19}NO_6S$ (365.39)	366 $(M+1)^+$
5j	89	amorphous	-18°	$C_{21}H_{21}NO_6S$ (414.45)	415 $(M+1)^+$
5k	95	oil	-83°	$C_{15}H_{19}NO_6S$ (341.37)	342 $(M+1)^+$
5l	90	amorphous	-17°	$C_{15}H_{18}N_2O_9S$ (402.37)	403 $(M+1)^+$
5m	95	amorphous	+15°	$C_{13}H_{18}N_2O_6S$ (330.35)	331 $(M+1)^+$

[a]Satisfactory microanalysis obtained for compounds **5**: C±0.28, H±0.26, N±0.24.

Table 4: ^{1}H NMR data for compounds **5**.

Compd.	^{1}H NMR (D_2O or DMSO-d_6+D_2O*) δ (ppm), *J* (Hz)
5a	2.75 (m, 1H, H-5), 3.61 (dd, 1H, $J_{5,6b}$= 4.6, H-6b), 3.71 (dd, 1H, $J_{5,6a}$= 2.6, $J_{6a,6b}$= 12.4, H-6a), 3.28 (ft, 1H, $J_{3,4}$= 10.4, H-3), 3.39 (ft, 1H, $J_{4,5}$= 10.4, H-4), 3.48 (ft, 1H, $J_{2,3}$= 10.4, H-2), 4.31 (d, 1H, $J_{1,2}$= 10.4, H-1), 7.44-7.65 (m, 5H, H_{Ar}).
5b	2.77 (m, 1H, H-5), 3.61 (dd, 1H, $J_{5,6b}$= 4.9, H-6b), 3.71 (dd, 1H, $J_{5,6a}$= 2.9, $J_{6a,6b}$= 12.7, H-6a), 3.28 (ft, 1H, $J_{3,4}$= 9.7, H-3), 3.37 (ft, 1H, $J_{4,5}$= 9.7, H-4), 3.45 (ft, 1H, $J_{2,3}$= 9.7, H-2), 4.28 (d, 1H, $J_{1,2}$= 9.7, H-1), 7.27 (ft, 2H, $J_{orthoH,H}$= 8.8, $J_{orthoH,F}$= 8.8, H_{Ar}), 7.56 (dd, 2H, $J_{metaH,F}$= 5.5, H_{Ar}).
5c	3.03 (m, 1H, H-5), 3.87 (dd, 1H, $J_{5,6b}$= 4.7, H-6b), 3.96 (dd, 1H, $J_{5,6a}$= 2.7, $J_{6a,6b}$= 12.3, H-6a), 3.53 (ft, 1H, $J_{3,4}$= 10.0, H-3), 3.64 (ft, 1H, $J_{4,5}$= 10.0, H-4), 3.71 (ft, 1H, $J_{2,3}$= 10.0, H-2), 4.15 (s, 3H, CH_3), 4.56 (d, 1H, $J_{1,2}$= 10.0, H-1), 7.24 (d, 2H, J= 8.2, H_{Ar}), 7.72 (d, 2H, J= 8.2, H_{Ar}).
5d*	2.52 (m, 1H, H-5), 3.29 (dd, 1H, $J_{5,6b}$= 6.0, H-6b), 3.51 (bd, 1H, $J_{6a,6b}$= 12.3, H-6a), 2.89-3.09 (m, 3H, H-2, H-3, H-4), 4.04 (d, 1H, $J_{1,2}$= 9.8, H-1), 7.84 (d, 2H, J= 8.7, H_{Ar}), 8.24 (d, 1H, J= 8.7, H_{Ar}).
5e*	2.59 (m, 1H, H-5), 2.91 (s, 6H, CH_3), 3.00-3.10 (m, 3H, H-2, H-3, H-4), 3.34 (bd, 1H, H-6b), 3.38 (bd, 1H, $J_{6a,6b}$= 12.0, H-6a), 4.07 (d, 1H, $J_{1,2}$= 9.7, H-1), 6.70 (d, 2H, J= 8.8, H_{Ar}), 7.34 (d, 2H, J= 8.8, H_{Ar}).
5f	2.86 (m, 1H, H-5), 3.85 (d, 2H, J= 3.6, H-6b, H-6a), 3.52 (ft, 1H, $J_{3,4}$= 10.0, H-3), 3.65 (ft, 1H, $J_{4,5}$= 10.0, H-4), 3.69 (ft, 1H, $J_{2,3}$= 10.0, H-2), 4.18 (s, 3H, CH_3), 4.43 (d, 1H, $J_{1,2}$= 9.4, H-1), 7.44 (t, 2H, J= 7.7, H_{Ar}), 7.50 (d, 1H, J= 7.7, H_{Ar}), 7.65 (dd, 1H, J= 7.7, H_{Ar}), 7.87 (dd, J= 7.7, H_{Ar}).
5g	2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.50 (m, 1H, H-5), 3.61 (d, 2H, J= 3.2, H-6b, H-6a), 3.23 (ft, 1H, $J_{3,4}$= 10.4, H-3), 3.43 (ft, 1H, $J_{4,5}$= 10.4, H-4), 3.44 (ft, 1H, $J_{2,3}$= 10.4, H-2) 3.86 (d, 1H, $J_{1,2}$= 10.4,

(continued)

Table 4 Continued

	H-1), 7.07 (s, 2H, H_{Ar}).
5h*	2.28 (m, 1H, H-5), 2.90 (ft, 1H, $J_{3,4}$= 9.5, H-3), 2.99 (ft, 1H, $J_{4,5}$= 9.5, H-2), 3.13 (ft, 1H, $J_{2,3}$= 9.5, H-4) 3.25 (dd, 1H, $J_{5,6b}$= 1.8, H-6b), 3.33 (dd, 1H, $J_{5,6a}$= 3.5, $J_{6a,6b}$= 11.8, H-6a), 3.51 (s, 3H, CH_3), 3.57 (d, 1H, $J_{1,2}$= 9.5, H-1), 3.65 (s, 6H, CH_3), 6.20 (s, 2H, H_{Ar}).
5i*	1.90 (m, 1H, H-5), 3.04 (bd, 1H, H-6b), 3.14 (dd, 1H, $J_{5,6a}$= 5.0, $J_{6a,6b}$= 11.6, H-6a), 2.65 (ft, 1H, $J_{3,4}$= 9.9, H-3), 2.97 (ft, 1H, $J_{4,5}$= 9.9, H-4), 2.98 (ft, 1H, $J_{2,3}$= 9.9, H-2), 3.56 (d, 1H, $J_{1,2}$= 9.5, H-1), 7.49-7.65 (m, 4H, H_{Ar}), 7.90-8.02 (m, 3H, H_{Ar}).
5j*	1.11 (m, 1H, H-5), 2.06 (bd, 1H, H-6b), 2.74 (bd, 1H, $J_{6a,6b}$= 10.7, H-6b), 2.41 (ft, 1H, $J_{3,4}$= 9.5, H-3), 2.91 (ft, 1H, $J_{4,5}$= 9.5, H-4), 2.96 (ft, 1H, $J_{2,3}$= 9.5, H-2), 3.31 (d, 1H, $J_{1,2}$= 9.5, H-1), 7.50-7.64 (m, 4H, H_{Ar}), 8.00-8.19 (m, 4H, H_{Ar}), 8.28 (s, 1H, H_{Ar}).
5k*	3.01-3.21 (m, 3H, H-2, H-3, H-4), 3.21 (m, 1H, H-5), 3.41 (dd, 1H, $J_{5,6b}$= 6.0, H-6b), 3.73 (bd, 1H, $J_{6a,6b}$= 12.0, H-6a), 4.63 (d, 1H, $J_{1,2}$= 9.8, H-1), 6.94 (d, 1H, $J_{8,9}$= 15.8, H-8), 7.03 (d, 1H, H-9), 7.25-7.37 (m, 3H, H_{Ar}), 7.59 (d, 2H, H_{Ar}).
5l	2.66 (m, 1H, H-5), 3.18 (ft, 1H, $J_{3,4}$= 9.2, H-3), 3.31 (ft, 1H, $J_{4,5}$= 9.2, H-4), 3.40 (ft, 1H, $J_{2,3}$= 9.2, H-2), 3.47 (d, 2H, $J_{5,6b}$= 3.5, H-6b, H-6a), 4.46 (d, 1H, $J_{1,2}$= 10.0, H-1), 7.13 (ft, 1H, J= 7.2, H-5i), 7.23 (ft, 1H, J= 7.2, H-6i), 7.60 (d, 1H, J= 8.2, H-7i), 7.74 (s, 1H, H-2i), 7.89 (d, 1H, J= 8.2, H-4i).
5m	2.85 (m, 1H, H-5), 3.65 (dd, 1H, $J_{5,6b}$= 5.0, H-6b), 3.75 (dd, 1H, $J_{5,6a}$= 1.4, $J_{6a,6b}$= 12.8, H-6a), 3.31 (ft, 1H, $J_{3,4}$= 9.9, H-3), 3.41 (ft, 1H, $J_{4,5}$= 9.9, H-4), 3.48 (ft, 1H, $J_{2,3}$= 9.9, H-2), 4.36 (d, 1H, $J_{1,2}$= 9.9, H-1), 6.93 (d, 2H, J= 8.2, H_{Ar}), 7.36 (d, 2H, J= 8.2, H_{Ar}).

The mixture was stirred at r.t. for 1 h, then acidified with 1N H_2SO_4 (20 mL). The organic layer was separated, washed with water (2 x 20 mL) and dried over magnesium sulfate. The solvent was concentrated and the crude product **4** was purified by chromatography (EP/AcOEt 7:3 to 1:1, except for **4h** CH_2Cl_2/MeOH 95:5).

Preparation of 4m. $SnCl_2$ (358 mg, 1.88 mmol) was added to a stirred solution of **4d** (200 mg, 0.36 mmol) in EtOH (10 mL) under nitrogen. After stirring 1 h at 75°C, aq 10% NaOH (30 mL) was added and the solution was extracted with CH_2Cl_2 (2 x 20 mL). The organic layer was dried ($MgSO_4$) then concentrated. The residue was purified by column chromatography (CH_2Cl_2/MeOH 85:15) giving **4m** (130 mg, 72% yield).

General procedure for the synthesis of desulfoglucosinolates 5a-m. A suspension of **4** (0.5 mmol) in dry MeOH (10 mL) was treated with 5 drops of 1M sodium methoxide solution at room temperature. The reaction was monitored by TLC. The reaction mixture was acidified with DOWEX 50 W ion-exchange resin (acid form), filtered and evaporated. The crude product **5** was chromatographed on a silica gel column (eluent CH_2Cl_2/MeOH 85:15).

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