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Glucosinolate Chemistry: Synthesis of *O*-Glycosylated Derivatives of Glucosinalbin

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The synthesis of the major glucosinolate of *Moringa oleifera* and of other non-natural *O*-glycosylated derivatives of glucosinalbin is reported. The synthetic sequence applied, which involves the conversion of carbohydrate-based nitrostyrenes into the key thiohydroximates, appears to be sufficiently versatile to synthesize a range of glucosinolates bearing a glycosylated phenolic function. We synthesized analogues of the naturally occurring L-rhamnoside **1** with a view to estimating the importance of this phenol-protecting sugar moiety in modulating the biological activity of the parent glucosinolate and related breakdown products.

Introduction

Most species within the order Brassicales have been shown to have significant effects on human health.[1,2] This is mainly due to secondary metabolites known as glucosinolates and their breakdown products, mainly isothiocyanates, oxazolidine-2-thiones and nitriles. Glucosinolates are naturally occurring thiosaccharidic compounds found in all families of Brassicales and can be hydrolysed by an atypical glucohydrolase called myrosinase (E.C. 3.2.1.147) to produce D-glucose and various compounds depending on the nature of the aglycon moiety.[3]

Moringa oleifera (horseradish tree) is a multipurpose tree that is used in a number of tropical countries[4] for human and animal feeding and medicinal purposes.[5,6] Owing to its bactericidal properties the plant is also currently employed for water purification.[7] *Moringa oleifera* extracts have also been tested as anticancer,[8] antiinflammatory and hepato-protective[9,10] agents. The seeds of the plant contain 8–10% of a structurally unusual glucosinolate (**1**), an *O*-rhamnosylated form of *p*-hydroxybenzyl glucosinolate, that is, glucosinalbin (**2**; Figure 1).

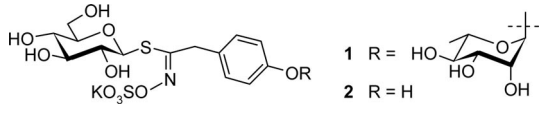

Figure 1. Glucosinalbin (**2**) and its glycosylated analogue **1** isolated from *Moringa oleifera*.

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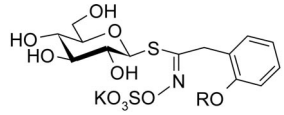
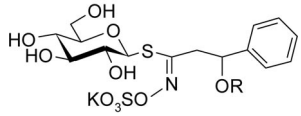
Compound **1** is a representative member of a restricted group of glucosinolates, the aglycon of which bears an *O*-glycosylated hydroxy function (Figure 2). The presence of a (4′-*O*-acetyl)-L-rhamnosyl analogue of **1** was postulated in *Moringa peregrina*[11] and other examples arise in the Resedaceae family: glucosinolate **3**, an *O*-rhamnosylated form of isoglucosinalbin **4**, was identified in the genus *Reseda*,[12] whereas **5**, an *O*-arabinosylated derivative of glucobarbarin **6**, was shown to be present in the genus *Sesamoides*.[13]



3 R = α-L-rhamnopyranosyl
4 R = H

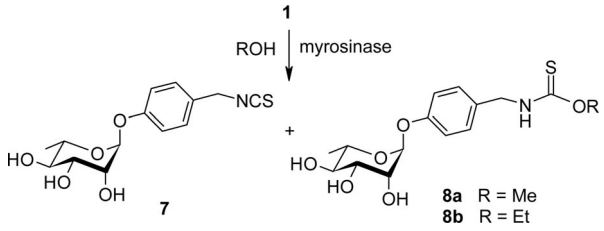


5 R = α-L-arabinopyranosyl
6 R = H

Figure 2. Other naturally occurring *O*-glycosylated glucosinolates.

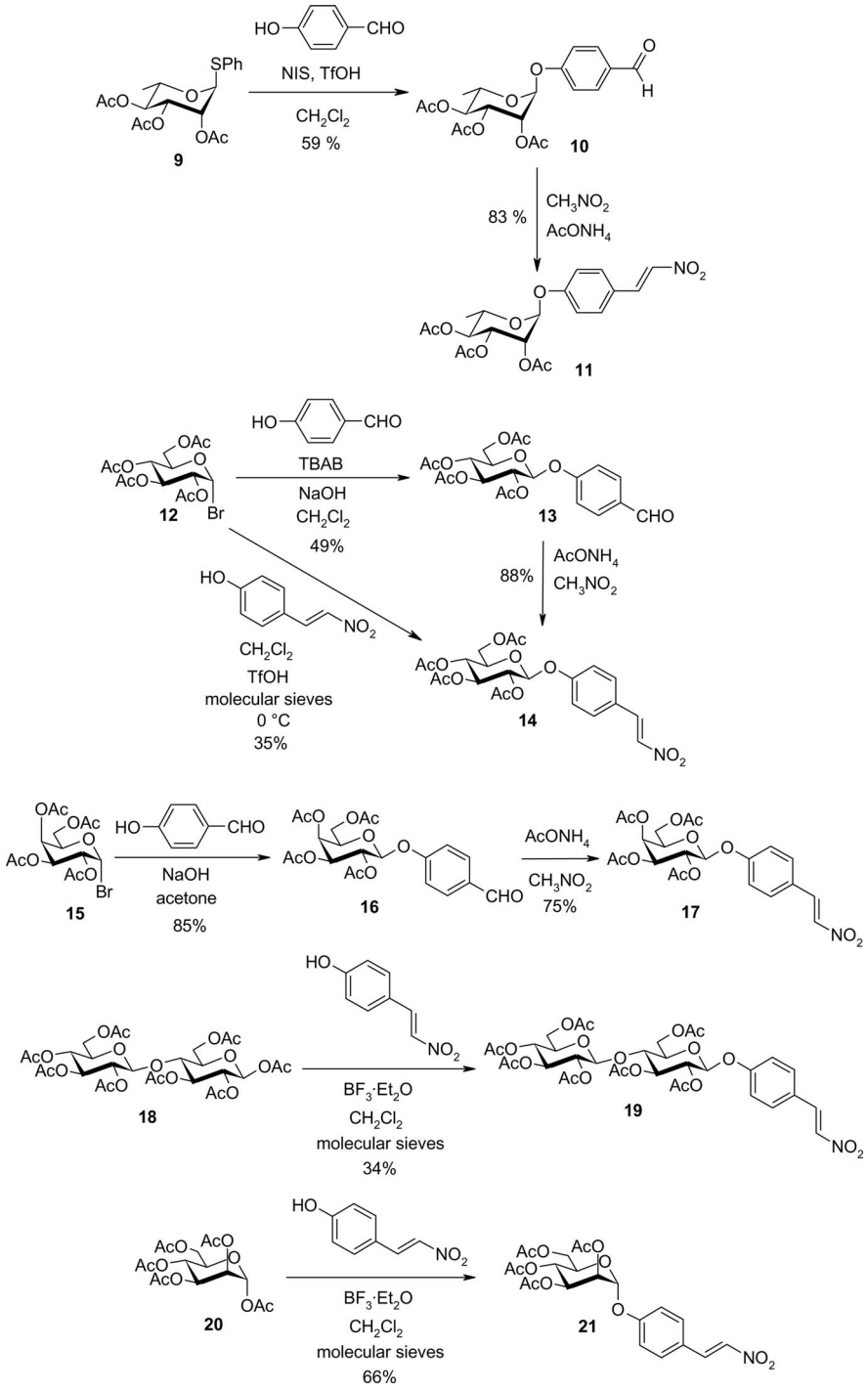
Glucosinolate **1** (sometimes called glucomoringin) can be hydrolysed by myrosinase to furnish a number of clearly identified bioactive compounds (Scheme 1).[14–16] Isothiocyanate **7** ("moringin") was recently shown to inhibit NF-kB and to reduce myeloma growth,[17] whereas related thionocarbamates **8a**,**b** have strong activity as hypotensive agents[15a] or antitumour promoters.[18]

Glucosinalbin is one of the few glucosinolates in which the aglycon chain bears a phenolic group. Bearing in mind the prominent position of phenol glycosides in the vegetable kingdom,[19] we planned to synthesize analogues of the nat-



Scheme 1. Bioactive compounds resulting from myrosinase hydrolysis of **1**.

urally occurring L-rhamnoside **1** with a view to estimating the importance of this phenol-protected sugar moiety in modulating the biological activity of the parent glucosinolate and the related breakdown products. In our earlier communication[20] we reported a synthesis of **1** involving the standard coupling of *O*-protected 1-thio-β-D-glucopyranose with the appropriate L-rhamnosylated hydroximoyl chloride. In this paper, we report the detailed synthesis of **1** and four *O*-glycosylated derivatives of glucosinalbin bearing a β-D-*gluco*, β-D-*galacto*, β-*cellobio* and α-D-*manno* unit.

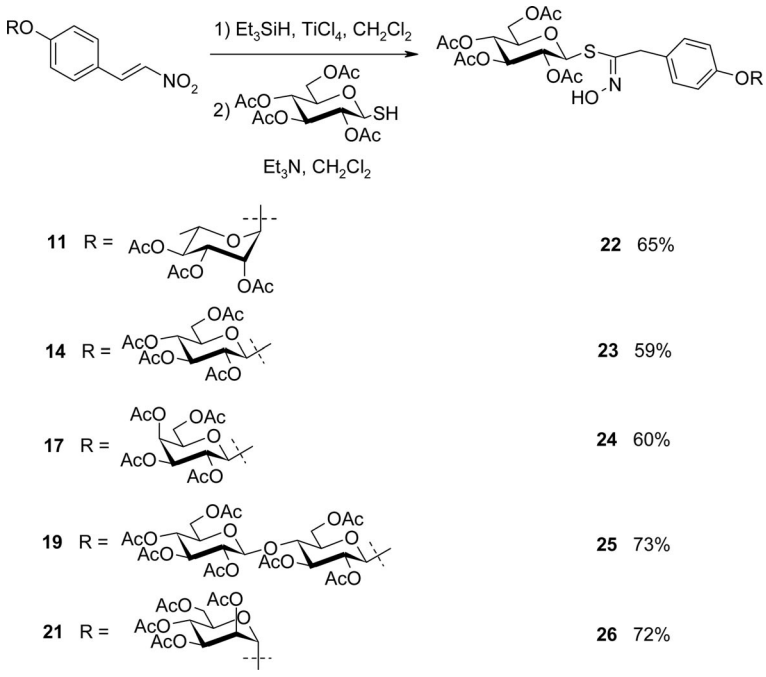


Scheme 2. Preparation of the nitrovinyl precursors.

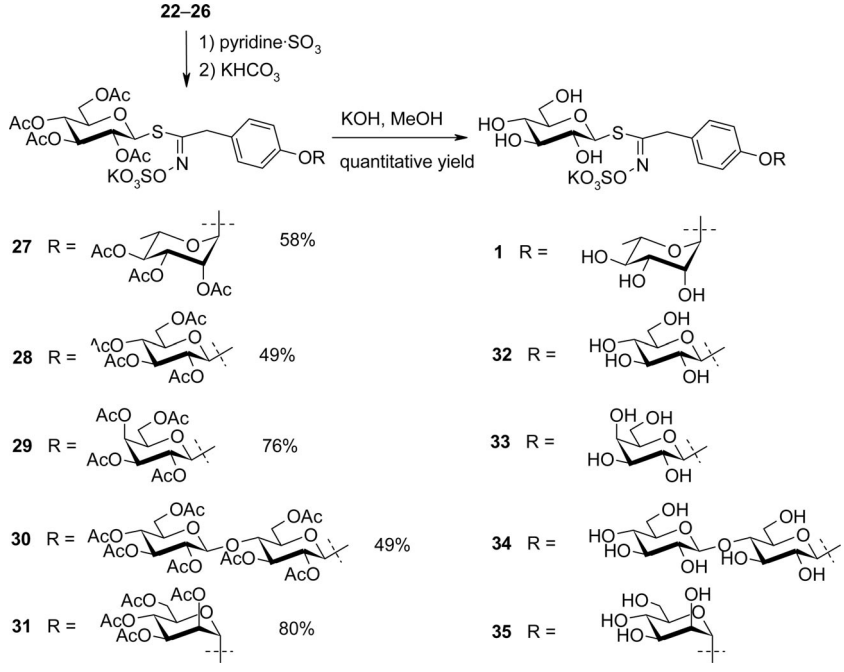
Results and Discussion

Our strategy requires the preparation of nitrostyrene precursors connected to sugar frameworks (Scheme 2). The previously described aryl α-L-rhamnoside **10**[21] was first obtained in nearly 60% yield from the corresponding thioglycoside **9**[22] through a slight modification of Leuck and Kunz's method.[23] Conversion of **10** into the nitrostyrene **11** was readily effected by using a variation of the Henry reaction.[24] Alternative protocols were used to prepare the other glycosides.

The glucose and galactose derivatives were obtained from α-bromo-glycosyl donors **12** and **15**, respectively, under standard conditions[25] to produce in moderate-to-good yields the *O*-glycoside aldehydes **13** and **16**, which were readily converted into nitrovinyl precursors **14** and **17**. The



Scheme 3. Preparation of the key thiohydroximates **22**–**26**.



Scheme 4. Synthesis of **1** and glucosinolates **32**–**35**.

cellobiose and mannose derivatives were prepared from per-*O*-acetates **18** and **20** by a classic Lewis acid-catalysed glycosylation[26] of *p*-hydroxy-2-nitrostyrene[24] to directly produce nitrovinyl precursors **19** and **21**, respectively, in rather low-to-moderate yields.

By submitting the nitrovinyl precursors to standard Kulkarni-type conditions,[27] the corresponding hydroximoyl chlorides were prepared and treated immediately with 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose under mildly basic conditions. The (*Z*)-thiohydroximates **22**–**26** were stereospecifically obtained in overall yields of 59–73% (Scheme 3).

Final conversion of the thiohydroximates **22**–**26** into the target glucosinolates **1** and **32**–**35** was performed according to a previously described protocol.[28] *O*-Sulfation of the hydroximino moiety with the sulfur trioxide–pyridine complex followed by quenching with aqueous potassium hydrogen carbonate afforded the per-*O*-acetylated glucosinolates **27**–**31**, which were readily deprotected under basic conditions to **1** and **32**–**35** (Scheme 4).

Conclusions

We have reported herein the synthesis of the major glucosinolate of *Moringa oleifera*, a promising tropical plant with a wide range of applications. By copying this nitrovinyl precursor approach, the synthesis was extended to other *O*-glycosylated derivatives of glucosinalbin with a view to estimating the influence of the phenol-protecting sugar moiety on the behaviour of the parent glucosinolate. Modulation of the bioactivity of these *O*-glycosylated glucosinalbins and the related breakdown products is under investigation.

Experimental Section

General: Anhydrous reactions were performed in predried flasks using anhydrous solvents (which were distilled when necessary according to a literature procedure[29]) under argon. All chemicals obtained from commercial suppliers were used without further purification. TLC was performed by using precoated aluminium-backed plates (Merck Kieselgel 60F254), which were visualized by UV light (254 nm) and by charring after exposure to a 5% H_2SO_4 solution in ethanol. Flash column chromatography was performed using silica gel (36–63 mesh, E. Merck). Melting points were determined with a Kofler hot-stage apparatus. Optical rotations were measured at 20 °C with a Perkin–Elmer 141 polarimeter. NMR spectra were recorded with a Bruker DPX 250 (250 MHz for ^{1}H and 62.89 MHz for ^{13}C) or AMX 500 (500 MHz for ^{1}H and 125.7 MHz for ^{13}C) spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from TMS. Coupling patterns in the ^{1}H NMR spectra are designated as s = singlet, d = doublet, t = triplet, q = quartet and m, multiplet and coupling constants are given in Hz. NMR peak assignments were established by NOESY, COSY, HSQC and HMBC methods for all reported compounds. Mass spectra were recorded with an API-300 spectrometer [Ionspray® (IS) or heated nebulizer (HN) ionization mode]. HRMS were recorded with a MicrOTOF-QII spectrometer (ESI mode).

4-(2′,3′,4′-Tri-*O*-acetyl-α-L-rhamnopyranosyloxy)benzaldehyde (10): Compound **10** was prepared in 59% yield from phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside and *p*-hydroxybenzaldehyde using a slight modification of the pent-4-enyl thioglycoside procedure previously described by Leuck and Kunz.[23]

Typical Procedure for the Synthesis of the *p*-Nitrostyryl Glycosides 11, 14 and 17: A mixture of **10** (0.085 g, 0.215 mmol) and dry ammonium acetate (0.018 g, 1.1 equiv.) in nitromethane (3 mL) was stirred under reflux for 2 h and then the solvent was evaporated under reduced pressure. Chromatographic purification (petroleum ether/AcOEt, 7:3) of the residue provided the nitrostyryl derivative **11**.

(*E*)-*p*-(2′,3′,4′-Tri-*O*-acetyl-α-L-rhamnopyranosyloxy)-2-nitrostyrene (11): Yellow syrup (0.078 g, 83%). $[\alpha]_D$ = –111 (*c* 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (d, $J_{6a,5}$ = 6.2 Hz, 3 H, 6-H), 2.01, 2.04, 2.18 (3 s, 9 H, CH_3CO), 3.91 (m, 1 H, 5-H), 5.15 (t, J_{vic} = 9.8 Hz, 1 H, 4-H), 5.40–5.51 (m, 3 H, 1-H, 2-H, 3-H), 7.13 (d, J_{vic} = 8.9 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.51 (d, J_{vic} = 8.9 Hz, 2 H, 3-H_{ar}, 5-H_{ar}), 7.53 (d, J_{vic} = 13.6 Hz, 1 H, 2-H_{vinyl}), 7.95 (d, J_{vic} = 13.6 Hz, 1 H, 1-H_{vinyl}) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 17.8 (C-6), 21.1, 21.2, 21.4 (CH_3CO), 68.0 (C-5), 69.1, 69.8 (C-2, C-3), 71.0 (C-4), 95.8 (C-1), 117.5 (aryl C-2, C-6), 124.9 (aryl C-4), 131.5 (aryl C-3, C-5), 136.3, 138.8 (vinyl C-1, C-2), 159.1 (aryl C-1), 170.3, 170.5 (CH_3CO) ppm. MS (IS+): *m*/*z* = 438 $[M + H]^+$, 455 $[M + NH_4]^+$, 460 $[M + Na]^+$, 476 $[M + K]^+$. HRMS (ESI): calcd. for $C_{20}H_{23}NNaO_{10}$ 460.1214; found 460.1198.

(*E*)-*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-nitrostyrene (14): Yellow solid (0.481 g, 88%); m.p. 166–168 °C (EtOH). $[\alpha]_D$ = –24 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04, 2.06, 2.07 (3 s, 12 H, CH_3CO), 3.91 (m, 1 H, 5-H), 4.18 (dd, $J_{6b,5}$ = 2.3, $J_{6a,6b}$ = 12.0 Hz, 1 H, 6b-H), 4.29 (dd, $J_{6a,6b}$ = 12.0, $J_{6a,5}$ = 5.3 Hz, 1 H, 6a-H), 5.11–5.36 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 7.20 (d, J_{vic} = 8.8 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.51 (d, J_{vic} = 8.8 Hz, 2 H, 3-H_{ar}, 5-H_{ar}), 7.53 (d, J_{vic} = 13.5 Hz, 1 H, 2-H_{vinyl}), 7.97 (d, J_{vic} = 13.5 Hz, 1 H, 1-H_{vinyl}) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 20.9 (CH_3CO), 61.9 (C-6), 68.6 (C-4), 71.1 (C-2), 72.3, 72.6 (C-3, C-5), 98.3 (C-1), 117.5 (aryl C-2, C-6), 125.0 (aryl C-4), 131.0 (aryl C-3, C-5), 136.2, 138.3 (vinyl C-1, C-2), 159.6 (aryl C-1), 169.3, 169.4, 170.2, 170.5 (CH_3CO) ppm. MS (IS^+): *m*/*z* = 513.5 $[M + NH_4]^+$, 518.5 $[M + Na]^+$, 534.5 $[M + K]^+$. HRMS (ESI): calcd. for $C_{22}H_{25}NNaO_{12}$ 518.1269; found 518.1251.

(*E*)-*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-galactopyranosyloxy)-2-nitrostyrene (17): Yellow syrup (0.324g, 75%). $[\alpha]_D$ = +7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.01, 2.03, 2.05, 2.18 (4 s, 12 H, CH_3CO), 4.06–4.26 (m, 3 H, 5-H, 6-H), 5.10–5.16 (m, 2 H, 1-H, 3-H), 5.46–5.54 (m, 2 H, 2-H, 4-H), 7.05 (d, J_{vic} = 8.8 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.50 (d, J_{vic} = 8.8 Hz, 2 H, 3-H_{ar}, 5-H_{ar}), 7.53 (d, J_{vic} = 13.6 Hz, 1 H, 2-H_{vinyl}), 7.97 (d, J_{vic} = 13.6 Hz, 1 H, 1-H_{vinyl}) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.6, 20.7, 21.0 (CH_3CO), 61.3 (C-6), 66.7 (C-4), 68.4 (C-2), 69.6 (C-3), 71.3 (C-5), 98.7 (C-1), 117.4 (aryl C-2, C-6), 125.0 (aryl C-4), 131.0 (aryl C-3, C-5), 136.1, 138.3 (vinyl C-1, C-2), 159.6 (aryl C-1), 169.3, 170.1, 170.3 (CH_3CO) ppm. MS (IS^+): *m*/*z* = 518.5 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{22}H_{25}NNaO_{12}$ 518.1269; found 518.1253.

Typical Procedure for the Synthesis of the *p*-Nitrostyryl Glycosides 19 and 21: $BF_3{\cdot}Et_2O$ (0.75 mL, 4 equiv.) was added to a solution of 1,2,3,6,2′,3′,4′,6′-octa-*O*-acetyl-β-cellobiose (1.00 g, 1.47 mmol) and commercial *p*-hydroxy-2-nitrostyrene (0.243 g, 1 equiv.) in dichloromethane (10 mL) and the reaction mixture was stirred for 3 d at room temperature. After hydrolysis and extraction of the aqueous phase with dichloromethane (×3), the combined organic layers were dried with magnesium sulfate and the solvent was evap-

orated under reduced pressure. Chromatographic purification (CH_2Cl_2/MeOH, 19:1) of the residue provided compound **19**.

(*E*)-*p*-(2′,3′,6′,2″,3″,4″,6″-Hepta-*O*-acetyl-β-cellobiosyloxy)-2-nitrostyrene (19): Yellow solid (0.387 g, 34%); m.p. 218–220 °C (EtOH). $[\alpha]_D$ = –23 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99, 2.02, 2.05, 2.06, 2.09, 2.10 (6 s, 21 H, CH_3CO), 3.66 (m, 1 H, 5′-H), 3.82–3.92 (m, 2 H, 4′-H, 5″-H), 4.03–4.17 (m, 2 H, 6b′-H, 6b″-H), 4.39 (dd, $J_{6a'',5''}$ = 4.5, $J_{6a'',6b''}$ = 12.4 Hz, 1 H, 6a″-H), 4.54 (m, 2 H, 1″-H, 6a′-H), 4.95 (t, J_{vic} = 7.9 Hz, 1 H, 2″-H), 5.04–5.32 (m, 5 H, 1′-H, 2′-H, 3′-H, 3″-H, 4″-H), 7.02 (d, J_{vic} = 8.7 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.50 (d, 2 H, 3-H_{ar}, 5-H_{ar}), 7.53 (d, J_{vic} = 13.6 Hz, 1 H, 2-H_{vinyl}), 7.97 (d, J_{vic} = 13.6 Hz, 1 H, 1-H_{vinyl}) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.5, 20.7 (CH_3CO), 61.5, 61.8 (C-6′, C-6″), 67.7, 71.2, 71.6, 72.0, 72.3, 72.9, 73.1, 76.2 (C-2′, C-3′, C-4′, C-5′, C-2″, C-3″, C-4″, C-5″), 98.0, 100.8 (C-1′, C-1″), 117.4 (aryl C-2, C-6), 125.0 (aryl C-4), 130.9 (aryl C-3, C-5), 136.1, 138.2 (vinyl C-1, C-2), 159.5 (aryl C-1), 169.0, 169.3, 169.5, 169.7, 170.1, 170.2, 170.5 (CH_3CO) ppm. MS (IS$^+$): *m*/*z* = 801.5 [M + NH_4]$^+$, 806.5 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{34}H_{41}NNaO_{20}$ 806.2114; found 806.2138.

(*E*)-*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-mannopyranosyloxy)-2-nitrostyrene (21): Yellow solid (2.005 g, 66%); m.p. 164–166 °C (EtOH). $[\alpha]_D$ = +118 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.03, 2.05, 2.06, 2.21 (4 s, 12 H, CH_3CO), 4.01–4.10 (m, 2 H, 5-H, 6b-H), 4.27 (dd, $J_{6a,5}$ = 5.3, $J_{6a,6b}$ = 12.6 Hz, 1 H, 6a-H), 5.38 (t, $J_{3,4}$ = 10.2 Hz, 1 H, 4-H), 5.45 (dd, $J_{1,2}$ = 1.9, $J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 5.55 (dd, 1 H, 3-H), 5.59 (d, $J_{1,2}$ = 1.9 Hz, 1 H, 1-H), 7.16 (d, J_{vic} = 8.9 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.52 (d, 2 H, 3-H_{ar}, 5-H_{ar}), 7.54 (d, J_{vic} = 13.6 Hz, 1 H, 2-H_{vinyl}), 7.97 (d, J_{vic} = 13.6 Hz, 1 H, 1-H_{vinyl}) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.6, 20.8 (CH_3CO), 61.9 (C-6), 65.6 (C-4), 68.6 (C-3), 69.0 (C-2), 69.5 (C-5), 95.5 (C-1), 117.1 (aryl C-2, C-6), 124.8 (aryl C-4),130.9 (aryl C-3, C-5), 136.1, 138.2 (vinyl C-1, C-2), 158.4 (aryl C-1), 169.6, 169.9, 170.4 (CH_3CO) ppm. MS (IS$^+$): *m*/*z* = 496.5 [M + H]$^+$, 518.5 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{22}H_{25}NNaO_{12}$ 518.1269; found 518.1262.

Typical Procedure for the Synthesis of the Thiohydroximate Precursors 22–26: Triethylsilane (60 μL, 2.1 equiv.) and titanium tetrachloride (43 μL, 2.2 equiv.) were added. to a solution of *p*-nitrostyryl glycoside **11** (0.078 g, 0.178 mmol) in dichloromethane (10 mL). After 18 h stirring at room temperature, the reaction mixture was hydrolysed and the aqueous phase extracted with dichloromethane (×2). The combined organic layers were dried with magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was dissolved again in dichloromethane (10 mL) and then commercial 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (0.078 g, 1.2 equiv.) and triethylamine (0.075 mL, 3 equiv.) were successively added. After stirring for 1 h at room temperature, the solvent was evaporated in vacuo. Chromatographic purification (petroleum ether/AcOEt, 1:1) of the residue provided compound **22**.

***S*-[*p*-(2′,3′,4′-Tri-*O*-acetyl-α-L-rhamnopyranosyloxy)phenylacetohydroximoyl]-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (22):** White solid (0.091 g, 65%); m.p. 104–106 °C (Et_2O/petroleum ether, 1:1). $[\alpha]_D$ = –45 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, $J_{6',5'}$ = 6.2 Hz, 3 H, 6′-H), 1.97, 1.98, 2.02, 2.03, 2.04, 2.09, 2.19 (7 s, 21 H, CH_3CO), 3.54 (m, 1 H, 5-H), 3.91 (s, 2 H, CH_2Ar), 3.99–4.21 (m, 3 H, 6-H, 5′-H), 4.81 (d, $J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 4.93–5.08 (m, 3 H, 2-H, 3-H, 4-H), 5.16 (t, J_{vic} = 9.8 Hz, 1 H, 4′-H), 5.43–5.55 (m, 3 H, 1′-H, 2′-H, 3′-H), 7.07 (d, J_{vic} = 8.7 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.20 (d, J_{vic} = 8.7 Hz, 2 H, 3-H_{ar}, 5-H_{ar}), 8.41 (s, 1 H, NOH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 17.5 (C-6′), 20.5, 20.6, 20.7, 20.9 (CH_3CO), 38.0 (CH_2Ar), 62.2 (C-6), 67.2 (C-5′), 68.0 (C-4), 68.9, 69.7 (C-2′, C-3′), 70.0 (C-2), 70.9 (C-4′), 73.7 (C-3), 75.7 (C-5), 79.4 (C-1), 95.9 (C-1′), 116.9 (aryl C-2, C-6), 129.2 (aryl C-3, C-5), 129.9 (aryl C-4), 155.2 (aryl C-1), 169.1, 169.3, 170.1, 170.5 (CH_3CO, C-7) ppm. MS (IS$^+$): *m*/*z* = 786.5 [M + H]$^+$, 808.5 [M + Na]$^+$, 824.5 [M + K]$^+$. HRMS (ESI): calcd. for $C_{34}H_{43}NNaO_{18}S$ 808.2093; found 808.2058.

***S*-[*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)phenylacetohydroximoyl]-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (23):** White solid (0.332 g, 59%); m.p. 124–126 °C (Et_2O/petroleum ether, 1:1). $[\alpha]_D$ = –12 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97, 2.00, 2.02, 2.03, 2.04, 2.06, 2.07 (7 s, 24 H, CH_3CO), 3.54 (m, 1 H, 5-H), 3.89 (m, 3 H, 5′-H, CH_2Ar), 4.00–4.33 (m, 4 H, 6-H, 6′-H), 4.84 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.93–5.35 (m, 7 H, 2-H, 3-H, 4-H, 1′-H, 2′-H, 3′-H, 4′-H), 6.97 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 7.18 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 8.55 (s, 1 H, NOH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7 (CH_3CO), 38.0 (CH_2Ar), 61.9, 62.2 (C-6, C-6′), 70.0 (C-2), 68.0, 68.2, 71.1, 72.7 (C-4, C-2′, C-3′, C-4′), 72.0 (C-5′), 73.6 (C-3), 75.7 (C-5), 79.4 (C-1), 99.1 (C-1′) 117.5 (aryl C-2, C-6), 129.3 (aryl C-3, C-5), 130.6 (aryl C-4), 156.0 (aryl C-1), 169.1, 169.3, 169.4, 170.2, 170.3, 170.5, 170.6 (CH_3CO, C-7) ppm. MS (IS$^+$): *m*/*z* = 844.5 [M + H]$^+$, 866.5 [M + Na]$^+$, 882.5 [M + K]$^+$. HRMS (ESI): calcd. for $C_{36}H_{45}NNaO_{20}S$ 866.2148; found 866.2129.

***S*-[*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-galactopyranosyloxy)phenylacetohydroximoyl]-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (24):** Colourless syrup (0.205 g, 60%). $[\alpha]_D$ = –2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97, 2.00, 2.03, 2.05, 2.07, 2.17 (7 s, 24 H, CH_3CO), 3.53 (m, 1 H, 5-H), 3.89 (s, 2 H, CH_2Ar), 3.99–4.26 (m, 5 H, 5′-H, 6-H, 6′-H), 4.84 (d, $J_{1,2}$ = 9.8 Hz, 1 H, 1-H), 4.93–5.16 (m, 5 H, 2-H, 3-H, 4-H, 1′-H, 3′-H), 5.44–5.51 (m, 2 H, 2′-H, 4′-H), 6.98 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 7.18 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 8.65 (s, 1 H, N*O*H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 20.8, 21.0 (CH_3CO), 38.0 (CH_2Ar), 61.2, 62.1 (C-6, C-6′), 68.0 (C-4), 66.9 (C-4′), 68.7 (C-2′), 70.0 (C-2), 70.8 (C-3′), 71.0 (C-5′), 73.6 (C-3), 75.7 (C-5), 79.4 (C-1), 99.7 (C-1′), 117.5 (aryl C-2, C-6), 129.3 (aryl C-3, C-5), 130.5 (aryl C-4), 156.1 (aryl C-1), 169.1, 169.3, 169.5, 170.1, 170.2, 170.3, 170.5, 171.3 (CH_3CO, C-7) ppm. MS (IS$^+$): *m*/*z* = 844.5 [M + H]$^+$. HRMS (ESI): calcd. for $C_{36}H_{45}NNaO_{20}S$ 866.2148; found 866.2142.

***S*-[*p*-(2′,3′,6′,2″,3″,4″,6″-Hepta-*O*-acetyl-β-cellobiosyloxy)phenylacetohydroximoyl]-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (25):** White solid (0.527 g, 73%); m.p. 182–184 °C (Et_2O/petroleum ether, 1:1). $[\alpha]_D$ = –19 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95, 1.98, 1.99, 2.01, 2.04, 2.07, 2.08 (8 s, 33 H, CH_3CO), 3.49 (m, 1 H, 5-H), 3.66 (m, 1 H, 5″-H), 3.73–3.89 (m, 2 H, 4′-H, 5′-H), 3.86 (s, 2 H, CH_2Ar), 3.95–4.01 (m, 2 H, 6-H), 4.04–4.16 (m, 2 H, 6b′-H, 6b″-H), 4.36 (dd, $J_{6a'',5''}$ = 4.5, $J_{6a'',6b''}$ = 12.6 Hz, 1 H, 6a″-H), 4.49–4.53 (m, 2 H, 1″-H, 6a′-H), 4.79–5.29 (m, 10 H, 1-H, 2-H, 3-H, 4-H, 1′-H, 2′-H, 3′-H, 2″-H, 3″-H, 4″-H), 6.93 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 7.16 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 8.75 (s, 1 H, N*O*H) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.4, 20.5, 20.7 (CH_3CO), 37.9 (CH_2Ar), 61.4, 61.8, 62.1 (C-6, C-6′, C-6″), 67.6, 67.8, 69.9, 71.2, 71.4, 71.8, 72.3, 72.8, 73.5, 75.5, 76.2 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2″, C-3″, C-4″, C-5″), 79.2 (C-1), 98.7, 100.7 (C-1′, C-1″), 117.3 (aryl C-2, C-6), 129.1 (aryl C-3, C-5), 130.6 (aryl C-4), 155.8 (aryl C-1), 169.0, 169.2, 169.3, 169.5, 169.7, 170.0, 170.1, 170.2, 170.4, 170.5 (CH_3CO, C-7) ppm. MS (IS$^+$): *m*/*z* = 1132.5 [M + H]$^+$, 1149.5 [M + NH_4]$^+$, 1154.5 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{41}H_{61}NNaO_{28}S$ 1154.2993; found 1154.2942.

***S*-[*p*-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-mannopyranosyloxy)phenylacetohydroximoyl]-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (26):** White solid (0.859 g, 72%); m.p. 102–104 °C (Et_2O/petroleum ether, 1:1). $[\alpha]_D$ = +31 (*c* = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.93, 1.98, 2.00, 2.04, 2.17 (6s, 24 H, CH_3CO), 3.52 (m, 1 H, 5-H), 3.86 (s, 2 H, CH_2Ar), 3.95–4.29 (m, 5 H, 5′-H, 6-H, 6′-H), 4.75 (d, $J_{1,2}$ = 9.8 Hz, 1 H, 1-H), 4.88–5.03 (m, 3 H, 2-H, 3-H, 4-H), 5.36 (t, $J_{3',4'}$ = 10.0 Hz, 1 H, 4′-H), 5.43 (dd, $J_{2',3'}$ = 3.4 Hz, 1 H, 2′-H), 5.52 (d, $J_{1',2'}$ = 1.9 Hz, 1 H, 1′-H), 5.54 (dd, 1 H, 3′-H), 7.03 (d, J_{vic} = 8.7 Hz, 2 H, H_{ar}), 7.16 (d, J_{vic} = 8.7 Hz, 2 H, H_{ar}), 9.07 (s, 1 H, NOH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 20.9 (*C*H_3CO), 38.0 (*C*H_2Ar), 62.0, 62.3 (C-6, C-6′), 65.8 (C-4′), 68.1 (C-4), 68.9 (C-3′), 69.2 (C-2′), 69.3 (C-5′), 70.0 (C-2), 73.6 (C-3), 75.7 (C-5), 79.4 (C-1), 96.0 (C-1′), 116.9 (aryl C-2, C-6), 129.3 (aryl C-3, C-5), 130.2 (aryl C-4), 155.0 (aryl C-1), 169.1, 169.3, 169.8, 170.0, 170.2, 170.5, 170.6 (CH_3*C*O, C-7) ppm. MS (IS$^+$): *m*/*z* = 844.5 [M + H]$^+$, 866.5 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{36}H_{45}NNaO_{20}S$ 866.2148; found 866.2118.

Typical Procedure for the Synthesis of the *O*-Sulfated Thiohydroximates 27–31: Sulfur trioxide–pyridine complex (176 mg, 5 equiv.) was added to a solution of compound **22** (0.174 g, 0.221 mmol) in DMF (3 mL). After 18 h stirring at 50 °C the reaction mixture was treated with an aqueous solution of $KHCO_3$ (0.2 M, 5 mL) and then the solvents were evaporated in vacuo. Chromatographic purification (AcOEt/MeOH, 17:3) of the residue provided compound **27**.

Per-*O*-acetylated 4′-*O*-(α-L-Rhamnopyranosyl) Glucosinalbin (27): Amorphous solid (0.115 g, 58%). $[\alpha]_D$ = –19 (*c* = 1.0, MeOH). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.06 (d, $J_{6',5'}$ = 6.0 Hz, 3 H, 6′-H), 1.92, 1.93, 1.96, 2.03, 2.13 (5 s, 21 H, CH_3CO), 3.69–4.08 (m, 6 H, 5-H, 5′-H, 6-H CH_2Ar), 4.77–4.99 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 5.21–5.39 (m, 4 H, 1′-H, 2′-H, 3′-H, 4′-H), 7.11 (d, J_{vic} = 8.3 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.30 (d, J_{vic} = 8.3 Hz, 2 H, 3-H_{ar}, 5-H_{ar}) ppm. ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 18.0 (C-6′), 21.1, 21.2, 21.3, 21.5 (*C*H_3CO), 37.1 (*C*H_2Ar), 62.4 (C-6), 67.6 (C-5′), 68.5 (C-4), 69.3, 69.5 (C-2′, C-3′), 70.3 (C-2), 70.7 (C-4′), 73.6 (C-3), 75.1 (C-5), 79.9 (C-1), 95.9 (C-1′), 117.6 (aryl C-2, C-6), 130.3 (aryl C-3, C-5), 131.1 (aryl C-4), 154.9 (aryl C-1), 153.5 (C-7), 169.9, 170.0, 170.3, 170.5, 170.6, 170.8 (CH_3*C*O) ppm. MS (IS–): *m*/*z* = 864 [M – K]$^+$. HRMS (ESI): calcd. for $C_{34}H_{42}NO_{21}S_2$ 864.1696; found 864.1703.

Per-*O*-acetylated 4′-*O*-(β-D-Glucopyranosyl) Glucosinalbin (28): Colourless syrup (0.072 g, 49%). $[\alpha]_D$ = +31 (*c* = 0.4, MeOH). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.92, 1.93, 1.95, 1.96, 1.99, 2.00 (6 s, 24 H, CH_3CO), 3.76–4.25 (m, 8 H, 5-H, 5′-H, 6-H, 6′-H, CH_2Ar), 4.78–5.07 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 5.27–5.42 (m, 3 H, 2′-H, 3′-H, 4′-H), 5.53 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 6.97 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 7.29 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 21.1, 21.2, 21.3 (*C*H_3CO), 36.6 (*C*H_2Ar), 62.5 (C-6, C-6′), 68.5, 68.9, 70.4, 71.5, 72.8, 73.6, 75.1 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 79.2 (C-1), 98.0 (C-1′), 117.3 (aryl C-2, C-6), 130.4 (aryl C-3, C-5), 131.2 (aryl C-4), 153.4 (C-7), 156.2 (aryl C-1), 169.9, 170.0, 170.2, 170.4, 170.8 (CH_3*C*O) ppm. MS (IS–): *m*/*z* = 923 [M – K]$^+$. HRMS (ESI): calcd. for $C_{36}H_{44}NO_{23}S_2$ 922.1751; found 922.1764.

Per-*O*-acetylated 4′-*O*-(β-D-Galactopyranosyl) Glucosinalbin (29): White amorphous solid (0.138 g, 76%); m.p. 162–164 °C. $[\alpha]_D$ = –2 (*c* = 1.0, MeOH). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.92, 1.93, 1.96, 1.99, 2.02, 2.13 (7 s, 24 H, CH_3CO), 3.76 (m, 1 H, 5-H), 3.89–4.08 (m, 6 H, 6-H, 6′-H, CH_2Ar), 4.41 (m, 1 H, 5′-H), 4.77–4.94 (m, 2 H), 5.19–5.33 (m, 5 H), 5.43 (d, 1 H, 1-H), 6.96 (d, J_{vic} = 8.3 Hz, 2 H, H_{ar}), 7.28 (d, J_{vic} = 8.3 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 20.9, 21.0, 21.1, 21.2 (*C*H_3CO), 36.9 (*C*H_2Ar), 62.0, 62.2 (C-6, C-6′), 68.3 (C-4), 67.9, 69.0 (C-2′, C-4′), 70.2 (C-2), 70.9 (C-3′, C-5′), 73.5 (C-3), 75.0 (C-5), 79.0 (C-1), 98.5 (C-1′), 117.2 (aryl C-2, C-6), 130.3 (aryl C-3, C-5), 131.1 (aryl C-4), 156.1 (aryl C-1), 153.3 (C-7), 169.8, 169.9, 170.0, 170.2, 170.3, 170.6, 170.7 (CH_3*C*O) ppm. MS (IS–): *m*/*z* = 922.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{36}H_{44}NO_{23}S_2$ 922.1751; found 922.1762.

Per-*O*-acetylated 4′-*O*-(β-Cellobiosyl) Glucosinalbin (30): White amorphous solid (0.143 g, 49%); m.p. 172–174 °C. $[\alpha]_D$ = –14 (*c* = 1.0, MeOH). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.91, 1.92, 1.93, 1.96, 1.98, 1.99, 2.01, 2.06 (8 s, 33 H, CH_3CO), 3.63–4.00 (m, 10H, 4′-H, 5-H, 5′-H, 5′′-H, 6a-H, 6b-H, 6b′-H, 6b′′-H, CH_2Ar), 4.11–4.25 (m, 2 H, 6a′-H, 6a′′-H), 4.52 (dd, *J* = 9.7, *J* = 7.8 Hz, 1 H, 4′′-H), 4.65–4.86 (m, 5 H, 1-H, 2-H, 3-H, 4-H, 1′′-H), 5.09–5.21 (m, 4 H, 2′-H, 3′-H, 2′′-H, 3′′-H), 5.34 (d, $J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 6.82 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}), 7.15 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 20.3, 20.4, 20.5, 20.7 (*C*H_3CO), 37.4 (*C*H_2Ar), 61.5, 62.0 (C-6, C-6′, C-6′′), 67.7, 69.6, 70.5, 70.9, 71.2, 72.2, 72.8, 74.3, 76.5 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 78.4 (C-1), 96.9, 99.6 (C-1′, C-1′′), 116.3 (aryl C-2, C-6), 129.6 (aryl C-3, C-5), 130.4 (aryl C-4), 155.4 (aryl C-1), 152.6 (C-7), 169.1, 169.2, 169.5, 169.6, 170.0, 170.1, 170.3 (CH_3*C*O) ppm. MS (IS–): *m*/*z* = 1211 [M – K]$^+$. HRMS (ESI): calcd. for $C_{48}H_{60}NO_{31}S_2$ 1210.2596; found 1210.2600.

Per-*O*-acetylated 4′-*O*-(α-D-Mannopyranosyl) Glucosinalbin (31): White amorphous solid (0.187 g, 80%); m.p. 150–152 °C. $[\alpha]_D$ = +32 (*c* = 1.0, MeOH). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.92, 1.93, 1.94, 1.99, 2.02, 2.13 (6 s, 24 H, CH_3CO), 3.70 (m, 1 H, 5-H), 3.91–4.18 (m, 7 H, CH_2Ar, 5′-H, 6-H, 6′-H), 4.76–4.94 (m, 2 H), 5.13–5.33 (m, 5 H), 5.70 (s, 1 H, 1′-H), 7.12 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}); 7.30 (d, J_{vic} = 8.5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 20.2, 20.3, 20.4, 20.6 (*C*H_3CO), 36.3 (*C*H_2Ar), 61.3 (C-6, C-6′), 65.2 (C-4′), 67.7 (C-4), 68.4 (C-3′), 68.5 (C-2′), 68.6 (C-5′), 69.5 (C-2), 72.7 (C-3), 74.2 (C-5), 78.4 (C-1), 95.4 (C-1′), 116.9 (aryl C-2, C-6), 129.5 (aryl C-3, C-5), 130.5 (aryl C-4), 154.1 (aryl C-1), 152.5 (C-7), 169.1, 169.2, 169.5, 169.6, 169.6, 169.9 (CH_3*C*O) ppm. MS (IS–): *m*/*z* = 922.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{36}H_{44}NO_{23}S_2$ 922.1751; found 922.1757.

Typical Procedure for the De-*O*-acetylation of Glycosylated Glucosinalbins. Synthesis of 1 and 32–35: A catalytic amount of potassium hydroxide was added to a solution of compound **27** (0.089 g, 0.098 mmol) in methanol (5 mL). After standing at room temperature for 4 h, the reaction mixture was neutralized by the addition of Dowex H$^+$ resin. After filtration, the solvent was evaporated in vacuo. Chromatographic purification of the residue on C-18 silica gel (eluent: water) followed by freeze-drying provided compound **1**.

4′-*O*-(α-L-Rhamnopyranosyl) Glucosinalbin (1): Amorphous solid (0.060 g, quantitative yield). $[\alpha]_D$ = –47 (*c* = 1.0, H_2O). ^1H NMR (500 MHz, D_2O): δ = 1.26 (d, $J_{6',5'}$ = 5.8 Hz, 3 H, 6′-H), 3.26 (m, 1 H, 5-H), 3.32–3.48 (m, 3 H, 2-H, 3-H, 4-H), 3.55 (t, J_{vic} = 9.7 Hz, 1 H, 4′-H), 3.64–3.72 (m, 2 H, 6-H), 3.83 (m, 1 H, 5′-H), 4.03 (dd, $J_{2',3'}$ = 3.5 Hz, 1 H, 3′-H), 4.13 (s, 2 H, CH_2Ar), 4.20 (dd, $J_{1',2'}$ = 1.9 Hz, 1 H, 2′-H), 4.74 (m, 1 H, 1-H), 5.58 (br. s, 1 H, 1′-H), 7.18 (d, J_{vic} = 8.5 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.40 (d, J_{vic} = 8.0 Hz, 2 H, 3-H_{ar}, 5-H_{ar}) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 18.2 (C-6′), 39.0 (*C*H_2Ar), 61.8 (C-6), 70.2 (C-4), 70.9 (C-5′), 71.5 (C-2′), 71.6 (C-3′), 73.3 (C-2), 73.5 (C-4′), 78.5 (C-3), 81.3 (C-5), 82.9 (C-1), 99.6 (C-1′), 119.1 (aryl C-2, C-6), 130.9 (aryl C-3, C-5), 130.9 (aryl C-4), 156.2 (aryl C-1), 164.2 (C-7) ppm. MS (IS–): *m*/*z* = 570.5

[M – K]$^+$. HRMS (ESI): calcd. for $C_{20}H_{28}NO_{14}S_2$ 570.0957; found 570.0939.

4′-*O*-(β-D-Glucopyranosyl) Glucosinalbin (32): Amorphous solid (0.097 g, quantitative yield). $[\alpha]_D$ = –11 (*c* = 1.0, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 3.26 (m, 1 H, 5-H), 3.33–3.40 (m, 2 H, 2-H, 3-H), 3.44 (t, J_{vic} = 8.7 Hz, 1 H, 4-H), 3.54 (t, J_{vic} = 9.3 Hz, 1 H, 4′-H), 3.61 (t, J_{vic} = 7.7 Hz, 1 H, 2′-H), 3.64–3.68 (m, 4 H, 6-H, 3′-H, 5′-H), 3.79 (dd, J_{gem} = 12.4, J_{vic} = 5.4 Hz, 1 H, 6b′-H), 3.96 (d, J_{gem} = 12.4 Hz, 1 H, 6a′-H), 4.14 (s, 2 H, CH_2Ar), 4.75 (d, J_{vic} = 9.0 Hz, 1 H, 1-H), 5.15 (d, J_{vic} = 7.5 Hz, 1 H, 1′-H), 7.18 (d, J_{vic} = 8.4 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.39 (d, J_{vic} = 8.4 Hz, 2 H, 3-H_{ar}, 5-H_{ar}) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 39.0 (*C*H_2Ar), 61.5 (C-6), 61.9 (C-6′), 70.4 (C-4), 70.9 (C-4′), 73.3 (C-2), 74.4 (C-2′), 77.0 (C-3′), 77.5 (C-5′), 78.4 (C-3), 81.1 (C-5), 82.7 (C-1), 101.6 (C-1′), 118.5 (aryl C-2, C-6), 131.0 (aryl C-3, C-5), 131.1 (aryl C-4), 157.4 (aryl C-1), 164.2 (C-7) ppm. MS (IS–): *m*/*z* = 586.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{20}H_{28}NO_{15}S_2$ 586.0906; found 586.0895.

4′-*O*-(β-D-Galactopyranosyl) Glucosinalbin (33): Amorphous solid (0.097 g, quantitative yield). $[\alpha]_D$ = –24 (*c* = 1.0, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 3.28 (m, 1 H, 5-H), 3.35–3.42 (m, 2 H, 2-H, 3-H), 3.45 (t, J_{vic} = 9.2 Hz, 1 H, 4-H), 3.69 (s, 2 H, 6-H), 3.83–3.87 (m, 3 H, 2′-H, 6′-H), 3.91 (m, 1 H, 5′-H), 4.06 (s, 1 H, 4′-H), 4.14–4.19 (m, 3 H, 3′-H, CH_2Ar), 4.77 (d, J_{vic} = 9.0 Hz, 1 H, 1-H), 5.10 (d, J_{vic} = 7.1 Hz, 1 H, 1′-H), 7.20 (d, J_{vic} = 8.0 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.40 (d, J_{vic} = 8.0 Hz, 2 H, 3-H_{ar}, 5-H_{ar}) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 39.0 (*C*H_2Ar), 61.8 (C-6), 62.3 (C-6′), 67.3, 70.0 (C-2′, C-4′), 70.2 (C-4), 73.3 (C-2), 74.0 (C-3′), 76.8 (C-5′), 78.4 (C-3), 81.3 (C-5), 82.8 (C-1), 102.2 (C-1′), 118.5 (aryl C-2, C-6), 131.0 (aryl C-3, C-5), 157.5 (aryl C-1), 164.2 (C-7) ppm. MS (IS–): *m*/*z* = 586.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{20}H_{28}NO_{15}S_2$ 586.0906; found 586.0891.

4′-*O*-(β-Cellobiosyl) Glucosinalbin (34): Amorphous solid (0.106 g, quantitative yield). $[\alpha]_D$ = –40 (*c* = 1.0, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 3.23 (m, 1 H, 5-H), 3.32–3.35 (m, 3 H, 2-H, 3-H, 2′′-H), 3.39–3.45 (m, 2 H, 4-H, 4′′-H), 3.50–3.55 (m, 2 H, 3′′-H, 5′′-H), 3.63 (m, 3 H, 6-H, 2′-H), 3.73–3.77 (m, 4 H, 3′-H, 4′-H, 5′-H, 6b′′-H), 3.88 (dd, J_{gem} = 11.7, J_{vic} = 2.3 Hz, 1 H, 6b′-H), 3.93 (dd, J_{gem} = 12.3, J_{vic} = 2.0 Hz, 1 H, 6a′′-H), 4.00 (d, J_{gem} = 11.7 Hz, 1 H, 6a′-H), 4.11 (s, 2 H, CH_2Ar), 4.55 (d, $J_{1'',2''}$ = 7.9 Hz, 1 H, 1′′-H), 4.72 (m, 1 H, 1-H), 5.15 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 7.16 (d, J_{vic} = 8.7 Hz, 2 H, 2-H_{ar}, 6-H_{ar}), 7.40 (d, J_{vic} = 8.7 Hz, 2 H, 3-H_{ar}, 5-H_{ar}) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 39.0 (*C*H_2Ar), 61.3 (C-6′), 61.7 (C-6), 62.1 (C-6′′), 70.2 (C-4), 70.9 (C-4′′), 73.3 (C-2), 74.2 (C-2′), 74.7 (C-2′′), 75.6 (C-4′), 76.4 (C-3′), 77.0 (C-3′′), 77.5 (C-5′′), 78.4 (C-3), 79.8 (C-5′), 81.3 (C-5), 82.9 (C-1), 101.5 (C-1′), 104.1 (C-1′′), 118.6 (aryl C-2, C-6), 130.9 (aryl C-3, C-5), 131.2 (aryl C-4), 157.4 (aryl C-1), 164.2 (C-7) ppm. MS (IS–): *m*/*z* = 748.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{26}H_{38}NO_{20}S_2$ 748.1434; found 748.1415.

4′-*O*-(α-D-Mannopyranosyl) Glucosinalbin (35): Amorphous solid (0.076 g, quantitative yield). $[\alpha]_D$ = –6 (*c* = 1.0, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 3.24 (m, 1 H, 5-H), 3.32 (m, 2 H, 2-H, 3-H), 3.41 (t, J_{vic} = 9.5 Hz, 1 H, 4-H), 3.65 (s, 2 H, 6-H), 3.73–3.81 (m, 4 H, 4′-H, 5′-H, 6′-H), 4.05 (dd, *J* = 3.2, *J* = 8.9 Hz, 1 H, 3′-H), 4.11 (s, 2 H, CH_2Ar), 4.17 (d, $J_{1',2'}$ = 0.9 Hz, 1 H, 2′-H), 4.70 (m, 1 H, 1-H), 5.62 (d, $J_{1',2'}$ = 0.9 Hz, 1 H, 1′-H), 7.19 (d, J_{vic} = 8.6 Hz, 2 H, H_{ar}), 7.37 (d, J_{vic} = 8.6 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 39.0 (*C*H_2Ar), 61.8 (C-6), 62.2 (C-6′), 68.1 (C-4′), 70.3 (C-4), 71.4 (C-2′), 71.9 (C-3′), 73.3 (C-2), 74.9 (C-5′), 78.5 (C-3), 81.4 (C-5), 82.9 (C-1), 99.9 (C-1′), 119.1 (aryl C-2, C-6), 130.9 (aryl C-4, C-3, C-5), 157.4 (aryl C-1), 164.2 (C-7) ppm. MS (IS+): *m*/*z* = 626 [M + H]$^+$, 648 [M + Na]$^+$, 664 [M + K]$^+$. MS (IS–): *m*/*z* = 586.5 [M – K]$^+$. HRMS (ESI): calcd. for $C_{20}H_{28}NO_{15}S_2$ 586.0906; found 586.0888.

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