Synthesis of novel hypotensive aromatic thiocarbamate glycosides

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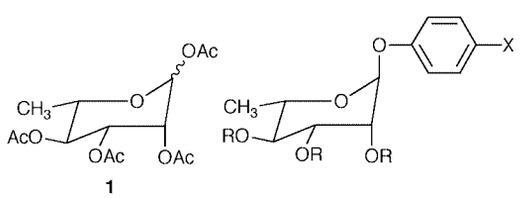
Syntheses of hypotensive thiocarbamate glycosides from *Moringa oleifera* are described. The route involves, first, the condensation of the sugar moiety with *p*-hydroxybenzonitrile to give glycoside **2**, then subsequent reduction of **2** to the glycosidic benzylamine **3**, which is then converted into isothiocyanate **6**. Finally, alcoholysis of **6** gives the desired thiocarbamate glycosides.

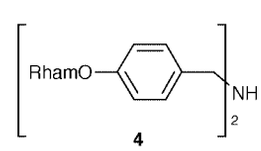
Thiocarbamate glycosides are rare in nature. They were first isolated in 1992 by S. Faizi *et al.* from a well known medicinal plant, *Moringa oleifera*, which is commonly found in Karachi, Pakistan.[1] These compounds exist in two stereoisomeric forms due to the barrier to rotation about the C–N bond, which has partial double-bond character.[1,2] Biological evaluation suggests that these glycosides are potent hypotensive,[3] antispasmodic[4] and antiviral[5] agents. Their paucity in nature and their significant pharmacological properties make them an attractive target for synthesis.

In this study, we have prepared some known glycosides, niazinin A **7** and niazimicin[1] **8**, as well as several analogues (**9**–**12**), in order to be able to explore the chemistry and biology of this group of compounds more extensively. Although both *E* and *Z* isomers of these glycosides appear to occur in nature,[1] the *E* isomers have been obtained predominantly in the present work. 4-(α-L-Rhamnosyloxy)benzylamine **3**, the corresponding dimeric secondary amine **4**, and the *N*,*O*-tetra-acetyl derivative **5** prepared in this study are new, although the *ortho* isomer of **3** has been reported from flowers of *Reseda odorata* and was synthesized in low yield.[6] 4-(α-L-Rhamnosyloxy)benzyl isothiocyanate **6**, formed on the way to the thiocarbamates and reported to be a potent antimicrobial agent,[7] is prepared for the first time.



1

	X	R
2	CN	Ac
3	CH_2NH_2	H
5	CH_2NHAc	Ac
6	CH_2NCS	H



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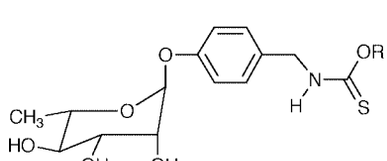

	R		R
7	CH_3	**11**	C_4H_9
8	C_2H_5	**12**	$H_2C{-}CH(CH_3)_2$
9	C_3H_7		
10	$HC(CH_3)_2$		

Results and discussion

The synthetic route followed in this work is outlined in Scheme 1. After acetylation of L-(+)-rhamnose,[8] the crude tetra-acetate **1** was condensed with *p*-hydroxybenzonitrile in the presence of a Lewis acid (zinc chloride) to give pure white, crystalline 4-(2′,3′,4′-tri-*O*-acetyl-α-L-rhamnosyloxy)benzonitrile **2** in 65–82% yield. Although zinc chloride usually gives α-D or β-L anomers predominantly, exceptions to this outcome are known.[8] Prior to this synthesis compound **2** had been prepared only through a multistep procedure.[9]

After trying many methods to reduce **2** to **3**, including catalytic hydrogenation at 40–60 psi† and reduction with $LiAlH_4$ (LAH)–H_2SO_4 (100%), sodium trifluoroacetoxyborohydride[10] was found to be a suitable reagent for this reduction. The formation of amine **3** is very slow, requiring 5–6 days to give crude product, which on HPLC affords **3** in 50% yield. Not unexpectedly, this reagent does not selectively reduce the nitrile group, but also brings about deacetylation of the sugar moiety.

The ^1H NMR spectrum of **3** showed an upfield shift for the aromatic protons at δ 7.02 and 7.28 (Table 1) as compared with the corresponding protons of **2** (Table 1), as well as a singlet at δ 3.82 for the benzylic methylene group (H_2-7). An HMQC spectrum showed connectivity of H-7 with the carbon atom at δ_C 53.11 (Table 3) which was recognized as a CH_2 in a DEPT ^{13}C NMR experiment. These chemical shifts, along with a downfield shift of C-4 compared with that observed in **2**,[9] and their agreement with the chemical shift observed for benzylamine,[11] confirm the structure of product **3**. The loss of three singlets for acetoxy methyls along with an MS fragment ion at *m*/*z* 147 demonstrated that deacetylation of the sugar moiety has taken place. EIMS, ESMS and CIMS of **3** did not show its

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† 1 psi = 6894.7 Pa.

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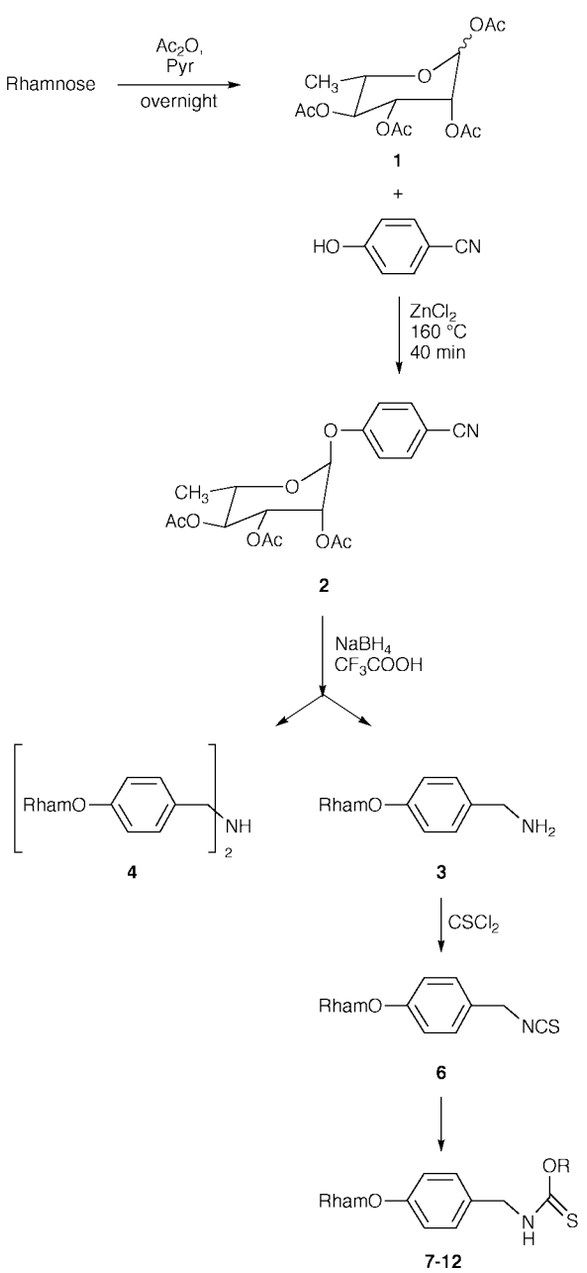
Table 1 ^{1}H NMR data of compounds **2**–**5**: coupling constants (*J*/Hz) in parentheses

Proton[a]	2	3	4	5
2,6	7.29d (8.8)	7.02d (8.4)	7.03d (8.8)	7.03d (8.8)
3,5	7.73d (8.8)	7.28d (8.4)	7.29d (8.8)	7.22d (8.8)
ArCH_2		3.82s	3.83br s	4.27d (6.4)
1′	5.75d (1.6)	5.45d (1.6)	5.45d (1.6)	5.56br s
2′	5.41dd (1.6, 3.6)	4.03dd (1.6, 3.6)	4.01dd (3.6, 1.6)	5.38m
3′	5.35dd (3.6, 10.0)	3.85dd (3.6, 9.2)	3.82dd (3.6, 9.2)	5.37dd (3.6, 9.2)
4′	5.08t (10.0)	3.46dd (9.2, 9.6)	3.48dd (9.2, 9.6)	5.07dd (9.2, 9.6)
5′	3.91qd (6.0, 10.0)	3.59dd (9.6, 6.4)	3.64qd (6.4, 9.6)	3.94qd (6.4, 9.6)
6′	1.11d (6.0)	1.13d (6.4)	1.17d (6.4)	1.11d (6.4)
NAc				1.88s
OAc	2.11, 2.01 1.83s			2.11, 2.01, 1.94s
NH				7.58 br s

[a] Unprimed locants refer to the aromatic ring; primed locants refer to the rhamnose moiety.



Scheme 1

molecular-ion peak. However, HRCIMS showed a fragment ion [corresponding to an $(M - NH_2)^+$ ion] at *m*/*z* 253.1072 (calc. for $C_{13}H_{17}O_5$: *m*/*z*, 253.1075). Formation of 4-(α-L-rhamnosyloxy)benzylamine **3** was confirmed by the preparation of its *N*,*O*-tetra-acetyl derivative **5**, HRCIMS of which showed a molecular ion peak at *m*/*z* 438.1768 (calc. for $C_{21}H_{28}NO_9$, $M^+ + 1$: *m*/*z*, 438.1764) (*vide infra*). The ^{1}H NMR spectrum of **5** further showed downfield shifts for the sugar moiety along with four singlets for the acetyl groups (three *O*-acetyl and one *N*-acetyl) at δ 2.11, 2.01, 1.94 and 1.88 (Table 1).

HPLC analysis of crude **3** showed a shoulder peak, which was identified through detailed spectral study as *N*,*N*-bis-4-(α-L-rhamnosyloxy)benzylamine **4** in 3% yield. The UV, IR and NMR spectral data for **4** were very similar to those for **3**. The only difference in the ^{1}H NMR spectra of the two compounds was in the multiplicity of the benzylic methylene (H-7) which appeared as a br s in **4** (converted into sharp singlet when shaken with D_2O) at δ 3.83 (Table 1). A molecular ion peak in the ESMS of **4** at *m*/*z* 522 ($M^+ + 1$) confirmed their structural assignment.

Equimolar quantities of 4-(α-L-rhamnosyloxy)benzylamine hydrochloride and thiophosgene react to give the corresponding isothiocyanate **6**, in 33–55% yield. Spectral data for **6** prepared in this way were comparable to those previously reported.[12] Thiocarbamate glycosides **7**–**12** were obtained in ≈20–40% yield when **6** was treated with sodium alkoxides. Spectral data of **7** (niazinin A) and **8** (niazimicin) were in full agreement with the literature values,[1] specific optical rotations of these compounds are reported here for the first time. Structures of naturally occurring thiocarbamate glycosidic analogues were established by detailed spectral studies (UV, IR, MS, NMR and 2D-NMR) (Tables 1 and 3) and comparison of data with literature values[1] for **7** and **8**.

Experimental

Mps were taken on a capillary apparatus and are uncorrected. UV (in MeOH) and IR (in CH_2Cl_2) spectra were recorded on a Hitachi U-2010 UV/VIS and a Perkin-Elmer 16 PC FTIR spectrophotometer, respectively. EIMS, CIMS and HRMS were recorded on a Micromass Autospec instrument, while electrospray data was collected on a VG Quattro instrument. NMR spectra were recorded in $(CD_3)_3CO$ on a Varian XL-400 instrument operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. HMQC and HMBC spectra were recorded on a UNITY-500 instrument. Specific optical rotations (in MeOH) were determined using a Perkin-Elmer 241 Polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. The ^{13}C NMR spectral assignments are based on DEPT, HMQC and HMBC experiments as well as on comparison with reported values for similar compounds.[1,9,11,12] Purity of compounds was checked on silica gel GF_{254} coated sheets. Reversed-phase high-performance liquid chromatography was performed using a semipreparative column (Supelco LC-18-BD; 25 cm × 10 mm; id 5 μm) (Supelco, Bellefonte, PA), a dual pump system (Waters M-45

Table 2 ^{1}H NMR data for glycosides **9**–**12**; coupling constants (*J*/Hz) in parentheses

Proton[a]	**9**	**10**	**11**	**12**
2,6	7.03d (8.8), 7.04d (8.8)	7.04d (8.8), 7.06d (8.8)	6.99d (8.8), 7.01d (8.8)	7.06d (8.8), 7.08d (8.4)
3,5	7.30d (8.8), 7.25d (8.8)	7.31d (8.8), 7.25d (8.8)	7.26d (8.4), 7.20d (8.4)	7.33d (8.8), 7.28d (8.4)
ArCH_2	4.71d (5.2), 4.41d (6.4)	4.71d (6.0), 4.38d (6.0)	4.67d (5.6), 4.35d (5.6)	4.73d (6.0), 4.45d (6.0)
1′	5.47br s	5.46d (1.6)	5.41d (1.6)	5.42br s
2′	4.02dd (3.2, 1.6)	4.03dd (3.2, 1.6)	3.96dd (3.6, 1.6)	3.98dd (3.6, 1.6)
3′	3.83dd (9.6, 3.2)	3.83dd (9.2, 3.2)	3.77dd (9.2, 3.6)	3.85dd (3.6, 9.6)
4′	3.49t (9.6)	3.49t (9.2)	3.43dd (9.6, 9.2)	3.51t (9.2)
5′	3.63qd (9.6, 6.0)	3.64qd (9.2, 6.4)	3.59qd (9.6, 6.4)	3.57qd (6.0, 9.6)
6′	1.18d (6.0), 1.17d (6.0)	1.19d (6.4), 1.18d (6.4)	1.13d (6.4), 1.12d (6.4)	1.21d (6.0), 1.20d (6.0)
1″	4.35t (6.4), 4.37t (6.4)	5.43hep (6.4), 5.41hep (6.4)	4.36t (6.4), 4.38t (6.4)	4.21d (6.4), 4.22d (6.4)
2″	1.68m, 1.67m	1.27d (6.4), 1.26d (6.4)	1.62quin (6.8)	2.03m
3″	0.85t (7.6), 0.81t (7.6)	1.27d (6.4), 1.26d (6.4)	1.34sextet (7.6), 1.24m	0.97d (6.8), 0.92d (6.8)
4″			0.87t (7.6), 0.85t (7.6)	0.97d (6.8), 0.92d (6.8)
NH	8.49br s	8.39br s	8.42br s	8.57br s

[a] Unprimed locants refer to the aromatic ring; primed locants refer to the rhamnose moiety; double-primed locants refer to the thiocarbamate ester group.

Table 3 ^{13}C NMR chemical shifts for glycosides **3**–**5** and **9**–**12**

Carbon[a]	**3**	**4**	**5**	**9**	**10**	**11**	**12**
1	156.70	156.56	156.04	158.86, 156.79	156.92, 156.80	156.93	156.91, 156.78
2,6	117.31	117.29	117.08	117.32, 117.40	117.36, 116.05	117.35, 117.41	117.34, 117.43
3,5	130.10	130.12	130.16	129.97, 129.71	130.00, 130.18	130.00, 129.71	130.01, 129.54
4	134.42	134.26	135.45	132.62, 132.79	132.71, 132.94	132.65	132.60, 132.81
ArCH_2	53.11	52.93	43.29	48.69, 46.57	48.56, 46.52	48.73, 46.61	48.72, 48.59
NC(S)OR				191.97, 190.5	191.14	192.01, 191.12	192.01, 190.53
1′	99.55	99.48	97.08	99.51, 99.48	99.56, 99.51	99.56	99.52, 99.48
2′	71.61	71.43	70.10	71.75	71.80	71.79	71.75
3′	72.12	71.97	70.47	72.23	72.34	72.34	72.29
4′	73.38	73.22	71.52	73.61	73.66	73.64	73.61
5′	70.19	70.15	68.42	70.21	70.25	70.24	70.21
6′	18.21	18.11	18.17	18.22	18.26	18.26	18.24
1″				72.19, 73.27	73.71	70.49, 71.50	76.75, 77.82
2″				22.83, 22.74	22.10, 21.99	31.64, 31.58	28.72, 28.67
3″				10.63, 10.72		19.82	19.35
4″						14.12	
5″							
6″							
7″							
NCOCH$_3$			170.45				
OCOCH$_3$			170.89, 170.78, 170.72				
NCOCH_3			21.03				
OCOCH_3			21.12, 21.08				

[a] Unprimed locants refer to the aromatic ring; primed locants refer to the rhamnose moiety; double-primed locants refer to the thiocarbamate ester group.

and 510 models), an L4000 Hitachi UV detector ($\lambda = 300$ nm), and an HP-3396A integrator. The flow was 2.5 ml min^{-1} and runs were monitored at $\lambda = 220$ nm (in case of **3**) and $\lambda = 245$ nm (in case of thiocarbamate glycosides).

MeOH 99.9% from Fisher Scientific and absolute EtOH from Pharmaco were used. Propan-1-ol, propan-2-ol, butan-1-ol and 2-methylpropan-1-ol from Fisher Scientific were further dried by refluxing with Mg turnings and iodine for 1–2 h and then distilled. Tetrahydrofuran from Mallinckrodt was distilled from potassium metal–benzophenone under argon.

Tetra-acetylation of L-(+)-rhamnose

To a solution of L-(+)-rhamnose monohydrate (1 g) in pyridine (3 ml) was added acetic anhydride (3 ml) and the reaction mixture was kept overnight at ambient temperature before being divided between ethyl acetate (100 ml) and water (100 ml). The aqueous phase was extracted thrice with ethyl acetate (150 ml) and the combined organic phase was washed thrice with water (300 ml), dried over $CaCl_2$ and evaporated under reduced pressure to give crude rhamnose tetra-acetate **1** (1.87 g, 92%).[8]

4-(2′,3′,4′-Tri-*O*-acetyl-α-L-rhamnosyloxy)benzonitrile 2

p-Hydroxybenzonitrile (1 g), rhamnose tetra-acetate **1** (1 g) and anhydrous zinc chloride (272 mg) were heated at 160 °C with stirring for 40 min. The melt after cooling was divided between benzene (130 ml) and 1 M NaOH (100 ml). The aqueous layer was extracted thrice with benzene (150 ml). The combined benzene phase was dried over $CaCl_2$ and evaporated on a Rotovap to give a yellow residue, which slowly converted into white crystals spontaneously (970 mg, 82%) (mp 63 °C; lit.,[9] 62 °C). The UV, IR, MS and NMR spectral data of these crystals agreed with those reported for 4-(2′,3′,4′-tri-*O*-acetyl-α-L-rhamnosyloxy)benzonitrile **2**.[9] The ^{1}H NMR spectrum of this product is reported in Table 1.

4-(α-L-Rhamnosyloxy)benzylamine 3 and bis derivative 4

To a stirred suspension of sodium borohydride (0.5 g, 13.2 mmol) in tetrahydrofuran (5 ml) was added trifluoroacetic acid (1.01 ml, 13.2 mmol in 10 ml of THF) over a period of 15 min at 0 °C under argon. To this solution of sodium trifluoroacetoxyborohydride was added compound **2** (0.5 g, 1.3 mmol in 5 ml of THF) in a dropwise manner. The mixture was stirred for one

day at room temperature and for another 4–5 days after the introduction of an additional amount of reagent (0.5 g of $NaBH_4$ and 1.01 ml of CF_3CO_2H). Excess of reagent was decomposed with saturated aq. NaCl (50 ml) at 0 °C, and two layers were separated. The THF layer was dried over Na_2SO_4 and evaporated under reduced pressure. A small part of the residue (200 mg/5 ml) was subjected to HPLC (mobile phase MeOH–H_2O 9:1), which showed three peaks. A broad peak 1 (t_R 3.73 min, 87 mg) remained unidentified; peak 2 (t_R 5.07 min) was identified as 4-(α-L-rhamnosyloxy)benzylamine **3** (101 mg, 50%; R_f 0.64, MeOH) and peak 3 (t_R 5.59 min) was recognized as *N*,*N*-bis[4-(α-L-rhamnosyloxy)benzyl]amine **4** (6.3 mg, 3%; R_f 0.61, MeOH).

4-(α-L-Rhamnosyloxy)benzylamine 3. $[\alpha]_D$ −33.75 (*c* 0.8); λ_{max}(MeOH)/nm 201, 222 and 265; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3400, 3100, 2900, 1640–1580, 1510, 1230 and 1150; HRCIMS (*m*/*z*) 253.1072 (Calc. for $C_{13}H_{17}O_5$: 253.1075, M − NH_2); ESMS (+ve) (*m*/*z*) 253; EIMS *m*/*z* (%) 253 (0.5), 147 (22), 129 (24), 107 (100) and 77 (17); ^{1}H and ^{13}C NMR in Tables 1 and 3.

***N*,*N*-Bis[4-(α-L-rhamnosyloxy)benzyl]amine 4.** $[\alpha]_D$ −13.88 (*c* 1.6); λ_{max}(MeOH)/nm 192, 224 and 270; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3050, 2950, 1630, 1580 and 1260; ESMS (+ve) (*m*/*z*) 522 (M^+ + 1); EIMS *m*/*z* (%) 485 (0.5), 269 (0.5), 253 (1), 239 (5), 211 (6), 147 (22), 133 (24), 129 (25) and 107 (100); ^{1}H and ^{13}C NMR in Tables 1 and 3.

N-Acetyl-4-[(2′,3′,4′-tri-*O*-acetyl)-α-L-rhamnosyloxy]-benzylamine 5

To a solution of **3** (25 mg) in pyridine (0.5 ml) was added acetic anhydride (0.5 ml) and the mixture was kept at room temperature overnight. Usual work-up gave pure acetyl derivative **5** as a white solid, mp 152–153 °C; R_f 0.52 ($CHCl_3$–MeOH 9:1); $[\alpha]_D$ −25 (*c* 1.2); λ_{max}(MeOH)/nm 224, 271; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3100, 2950, 1740, 1660, 1600, 1510, 1420, 1380, 1260 and 1230; HRCIMS (*m*/*z*) 438.1768 [calc. for $C_{21}H_{28}NO_9$: 438.1764 (M + 1)]; ESMS (+ve) (*m*/*z*) (%) 438 (M^+ + 1, 100), 396 (20), 379 (5), 273 (95), 231 (10), 213 (25), 153 (7) and 107 (4); ^{1}H and ^{13}C NMR data in Tables 1 and 3.

4-(α-L-Rhamnosyloxy)benzyl isothiocyanate 6

A solution of 4-(α-L-rhamnosyloxy)benzylamine hydrochloride (133 mg, 0.44 mmol) in H_2O (5 ml) was placed in a three-neck flask containing thiophosgene (33 μl, 0.44 mmol) in diethyl ether (10 ml) at 0 °C under argon.[13] To this reaction mixture was added dropwise 2.7 M sodium hydroxide (5 ml) with continuous stirring. Stirring was continued for a further 5 min. The two phases were then separated and the aqueous phase was extracted twice with diethyl ether (30 ml). The combined organic phase was evaporated under reduced pressure to give **6** as a yellow residue (72 mg, 53%).

General procedure for preparation of thiocarbamate glycosides

4-(α-L-Rhamnosyloxy)benzyl isothiocyanate **6** (50 mg) was refluxed with a freshly prepared sodium alkoxide (20 ml) for 30 min with continuous stirring. The reaction mixture was divided between water (10 ml) and ethyl acetate (20 ml). The aqueous phase was extracted thrice with ethyl acetate (30 ml). The combined organic layer was washed with an equal amount of water thrice, dried over $CaCl_2$, and concentrated under reduced pressure to give a crude product **7**–**12**, which was further purified by HPLC. Mobile phase used for compounds **7**, **10**–**12** was MeOH–H_2O (7:3) while that for glycosides **8** and **9** was MeOH–H_2O (1:1). HPLC of crude **7** gave pure niazinin A (29%; t_R 6.03 min); $[\alpha]_D$ −35 (*c* 1). Compound **8** on HPLC analysis gave niazimicin (22%; t_R 15.27 min); $[\alpha]_D$ −12 (*c* 1). HPLC of **9**–**12** gave pure glycosidic analogues in 24% [t_R 25.59 min; R_f 0.14 ($CHCl_3$–MeOH 9:1), **9**], 25% [t_R 6.76 min; R_f 0.14 ($CHCl_3$–MeOH 9:1), **10**], 33% [t_R 8.77 min; R_f 0.12 ($CHCl_3$–MeOH 9:1), **11**] and 38% [t_R 8.36 min; R_f 0.12 ($CHCl_3$–MeOH 9:1), **12**], yield respectively.

***O*-Propyl (*E*)-[4-(α-L-rhamnosyloxy)benzyl]thiocarbamate 9.** $[\alpha]_D$ −18 (*c* 1); λ_{max}(MeOH)/nm 205, 223, 245; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3400, 3100, 2900, 1600, 1500, 1400 and 1260; HREIMS (*m*/*z*) 371.1413 [calc. for $C_{17}H_{25}NO_6S$: 371.1402 (M)]; EIMS (*m*/*z*) (%) 371 (M^+, 0.3), 353 (0.5), 311 (1), 225 (30), 183 (22), 147 (10), 129 (12), 122 (15), 107 (100) and 77 (25). ^{1}H and ^{13}C NMR data in Tables 2 and 3.

***O*-Isopropyl (*E*)-[4-(α-L-rhamnosyloxy)benzyl]thiocarbamate 10.** $[\alpha]_D$ −18.88 (*c* 0.9); λ_{max}(MeOH)/nm 203, 220 and 245; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3400, 3100, 1600, 1520 and 1240; HREIMS (*m*/*z*) 371.1383 [calc. for $C_{17}H_{25}NO_6S$: 371.1402 (M)]; EIMS (*m*/*z*) (%) 371 (M^+, 10), 328 (4), 225 (40), 182 (100), 166 (6), 147 (13), 129 (15), 122 (22), 107 (75) and 77 (10). ^{1}H and ^{13}C NMR data in Tables 2 and 3.

***O*-Butyl (*E*)-[4-(α-L-rhamnosyloxy)benzyl]thiocarbamate 11.** $[\alpha]_D$ −47 (*c* 1); λ_{max}(MeOH)/nm 201, 220, 245; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3400, 3100, 1620, 1500, 1230; HREIMS (*m*/*z*) 385.1549 [calc. for $C_{18}H_{27}NO_6S$: 385.1559 (M)]; EIMS (*m*/*z*) (%) 385 (M^+, 15), 329 (1), 239 (75), 183 (85), 166 (17), 147 (19), 129 (26), 122 (30), 107 (100) and 77 (13). ^{1}H and ^{13}C NMR in Tables 2 and 3.

***O*-Isobutyl (*E*)-[4-(α-L-rhamnosyloxy)benzyl]thiocarbamate 12.** $[\alpha]_D$ −40 (*c* 1); λ_{max}(MeOH)/nm 205, 223 and 245; $\nu_{max}(CH_2Cl_2)$/nm 3400, 3100, 2900, 1620, 1510, 1420 and 1240; HREIMS (*m*/*z*) 385.1565 [calc. for $C_{18}H_{27}NO_6S$: 385.1559 (M)]; EIMS (*m*/*z*) (%) 385 (M^+, 7), 329 (12), 239 (18), 183 (100), 147 (28), 129 (27), 122 (15), 107 (75) and 77 (7). ^{1}H and ^{13}C NMR data in Tables 2 and 3.

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