Regular Article

Novel Steroidal Glycosides from the Whole Plants of *Helleborus foetidus*

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Received November 24, 2019; accepted December 12, 2019

Phytochemical analysis of the whole *Helleborus foetidus* plants identified 28 steroidal glycosides (1–28), including 20 novel spirostanol glycosides (1–20) and a novel furostanol glycoside (21). The structures of the newly identified compounds were elucidated by two-dimensional NMR spectroscopy and hydrolytic cleavage. Compounds 12, 13, and 15 were determined to be spirostanol trisdesmosides bearing sugar moieties at the C-1, -21, and -24 hydroxy groups of the aglycone unit. The isolated compounds were subsequently evaluated for cytotoxic activity against HL-60 human promyelocytic leukemia cells and A549 human lung carcinoma cells. In particular, 7 showed cytotoxic activity against the HL-60 and A549 cells, with IC_{50} values of 5.9 and 6.6 μM, respectively, whereas 19 was selectively cytotoxic to A549 cells with an IC_{50} value of 5.5 μM.

Key words *Helleborus foetidus*; Ranunculaceae; whole plant; steroidal glycoside; cytotoxic activity

Introduction

Plants from the genus *Helleborus* are perennials belonging to the Ranunculaceae family, and are widely distributed throughout Europe.[1] *Helleborus* species are poisonous plants and a series of bufadienolides have been isolated from *H. caucasicus*,[2,3] *H. odorus*,[4,5] *H. thibetanus*,[6–8] and *H. torquatus*.[9] Recently, various bufadienolides from *H. orientalis* and *H. foetidus* were isolated and identified, some of which showed significantly potent cytotoxic activity and induced apoptosis *via* a mitochondria dependent pathway in cultured tumor cells.[10,11] Because *Helleborus* species has been reported to concomitantly contain the glycoside derivatives of C_{27} steroids (spirostanols and furostanols),[12–18] further phytochemical examination of the methanolic extract of *H. foetidus* was performed using whole plants with a specific focus on steroidal glycosides. The isolation of 28 steroidal glycosides (**1**–**28**), including 20 novel spirostanol glycosides (**1**–**20**) and a novel furostanol glycoside (**21**) was achieved. The structures of the newly identified compounds were determined from their two-dimensional NMR spectra and hydrolytic cleavage. The cytotoxic activities of the isolated compounds were evaluated against HL-60 human promyelocytic leukemia cells and A549 human lung carcinoma cells.

Results and Discussion

Whole plants of *H. foetidus* (fresh weight, 3.3 kg) were extracted using hot MeOH. The concentrated MeOH extract (115 g) was fractionated using a Diaion HP-20 porous polymer polystyrene resin column with MeOH/H_2O (3 : 7), MeOH/H_2O (1 : 1), MeOH, EtOH, and EtOAc, successively (each solvent volume 6 L). The MeOH eluted fraction was subjected to silica gel column chromatography (CC), octadecylsilanized (ODS) silica gel CC, and preparative ODS HPLC to obtain 28 compounds (**1**–**28**). Previously characterized compounds (**22**–**28**) were identified as (23*S*,24*S*,25*S*)-24-[(β-D-fucopyranosyl)-oxy]-3β,23-dihydroxyspirost-5-en-1β-yl *O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside (**22**),[19] (23*S*,24*S*,25*S*)-24-[(β-D-fucopyranosyl)oxy]-3β,23-dihydroxyspirost-5-en-1β-yl *O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside (**23**),[19] (23*S*,24*S*)-3β,23,24-trihydroxyspirosta-5,25(27)-dien-1β-yl *O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside (**24**),[20] (23*S*,24*S*)-21-acetyloxy-3β,23,24-trihydroxyspirosta-5,25(27)-dien-1β-yl *O*-β-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside (**25**),[10] (25*R*)-26-[(β-D-glucopyranosyl)oxy]-1β,22α-dihydroxyfurost-5-en-3β-yl β-D-glucopyranoside (**26**),[21] (25*R*)-26-[(β-D-glucopyranosyl)oxy]-22α-hydroxyfurost-5-en-3β-yl *O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside (**27**),[22] and (25*S*)-22α,25-epoxy-26-[(β-D-glucopyranosyl)oxy]-3β-hydroxyfurost-5-en-1β-yl α-L-arabinopyranoside (**28**),[13] respectively (Fig. 1).

Compound **1** was obtained as an amorphous powder and its molecular formula was determined to be $C_{45}H_{70}O_{19}$, based on high resolution-electrospray ionization-time of flight (HR-ESI-TOF)-MS and ^{13}C-NMR spectra data. The IR spectrum of **1** showed absorption bands of hydroxy (3392 cm^{-1}) and carbonyl groups (1729 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra of **1** indicated the presence of four steroidal methyl groups [δ_H 1.35 (3H, s, Me-19), 1.13 (3H, d, J = 7.0 Hz, Me-21), 1.02 (3H, s, Me-18), and 0.97 (3H, d, J = 6.8 Hz, Me-27); δ_C 16.8 (C-18), 14.9 (C-19), 14.6 (C-21), and 13.0 (C-27)], an olefinic group [δ_H 5.60 (1H, brd, J = 5.8 Hz, H-6); δ_C 139.3 (C-5) and 124.9 (C-6)], an oxygenated methylene group [δ_H 3.82 (1H, dd, J = 11.2, 11.2 Hz, H-26ax) and 3.43 (1H, dd, J = 11.2, 4.7 Hz, H-26eq); δ_C 60.6 (C-26)], five oxygenated methine groups [δ_H 4.61 (1H, m, H-16), 4.10 (1H, brs, H-24), 3.90 (1H, m, H-3), 3.83 (1H, dd, J = 12.0, 4.1 Hz, H-1), and 3.81 (1H, d, J = 3.2 Hz, H-23); δ_C 84.0 (C-1), 83.0 (C-16), 73.0 (C-24), 68.7 (C-23), and 68.0 (C-3)], and an acetyl group [δ_H 2.01 (3H, s); δ_C 170.8 and 21.0]. Furthermore, signals corresponding to three anomeric protons and carbons were observed [δ_H 6.48 (1H, brs), 4.94 (1H, d, J = 7.6 Hz), and 4.69 (1H, d, J = 7.9 Hz); δ_C 106.7, 100.8, and 100.7]. The ^{1}H- and ^{13}C-NMR spectral data of **1** were similar to those obtained for **24**, except for the signals arising from the F-ring part of the steroidal skeleton. Instead of the ^{1}H- and ^{13}C-NMR signals arising from the C-25(27)

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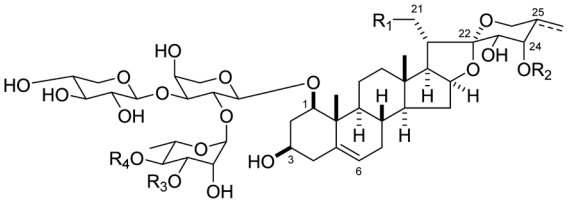
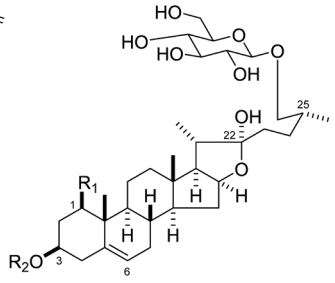
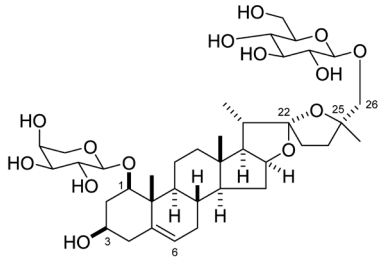


		R_1	R_2	R_3	R_4
1		H	H	H	Ac
2		H	Qui	H	Ac
3		H	H	Api	Ac
4		H	Fuc	Api	Ac
5		H	Glc	H	H
6		OH	H	H	Ac
7		OH	Fuc	H	Ac
8		OH	H	Api	Ac
9		OH	Ara	Api	Ac
10		OH	Fuc	Api	Ac
11		O-Gal	H	Api	Ac
12		O-Gal	Ara	Api	Ac
13		O-Gal^2-Glc	Fuc	H	H
14		O-Gal^2-Glc	H	Api	Ac
15		O-Gal^2-Glc	Fuc	Api	Ac
16	$\Delta^{25(27)}$	H	Fuc	Api	Ac
17	$\Delta^{25(27)}$	OH	H	Api	Ac
18	$\Delta^{25(27)}$	OH	Ara	Api	Ac
19	$\Delta^{25(27)}$	O-Ac	Ara	Api	Ac
20	$\Delta^{25(27)}$	O-Ac	Ara	H	Ac
22		H	Fuc	H	H
23		H	Fuc	H	Ac
24	$\Delta^{25(27)}$	H	H	H	Ac
25	$\Delta^{25(27)}$	O-Ac	H	Api	Ac



	R_1	R_2
21	O-Ara	H
26	OH	Glc
27	H	Glc^2-Rha



28

Fig. 1. Structures of Isolated Compounds **1**–**28**

Ara: α-L-arabinopyranosyl; Api: β-D-apiofuranosyl; Fuc: β-D-fucopyranosyl; Gal: β-D-galactopyranosyl; Glc: β-D-glucopyranosyl; Rha: α-L-rhamnopyranosyl; Qui: β-D-quinovopyranosyl; Ac: acetyl.

exomethylene group [δ_H 5.07 and 4.97 (each 1H, brs, H_2-27); δ_C 146.1 (C-25) and 112.3 (C-27)] observed in **24**, signals from a secondary methyl group [δ_H 0.97 (3H, d, $J = 6.8$ Hz, Me-27); δ_C 13.0 (C-27)] and methine group [δ_H 1.89 (1H, m, H-25); δ_C 36.1 (C-25)] were observed in the ^{1}H- and ^{13}C-NMR spectra of **1**. These data suggest that **1** is a saturated derivative of **24** in terms of the C-25(27) exomethylene group. Nuclear Overhauser effect spectroscopy (NOESY) of **1** was performed and NOE correlations were observed between H-23 (δ_H 3.81) and H-20 (δ_H 2.97)/H-24 (δ_H 4.10)/H-25 (δ_H 1.89) as well as between H-26ax (δ_H 3.82) and H-16 (δ_H 4.61). Additionally, the proton spin-coupling constants of $^3J_{H\text{-}23,H\text{-}24}$ and $^3J_{H\text{-}25,H\text{-}26ax}$ were 3.2 and 11.2 Hz, respectively. Thus, the configurations of C-23, C-24, and C-25 were determined as 23*S*, 24*S*, and 25*S*. Acid hydrolysis of **1** with 0.2 M HCl (dioxane/H_2O; 1 : 1) yielded L-arabinose, L-rhamnose, and D-xylose carbohydrate moieties. The ^{1}H-^{1}H correlation spectroscopy (COSY) and heteronuclear single quantum coherence (HSQC) spectra indicated that the sugar moiety of **1** comprised a 2,3-disubstituted inner α-L-arabinopyranosyl unit [Ara: δ_H 4.69 (1H, d, $J = 7.9$ Hz, H-1′); δ_C 100.8, 72.8, 85.2, 69.9, and 67.3 (C-1′–5′)], a terminal α-L-rhamnopyranosyl unit [Rha: δ_H 6.48 (1H, brs, H-1″); δ_C 100.7, 72.2, 69.9, 76.5, 66.5, and 18.5 (C-1″–6″)], and a terminal β-D-xylopyranosyl unit [Xyl: δ_H 4.94 (1H, d, $J = 7.6$ Hz, H-1‴); δ_C 106.7, 74.5, 78.5, 70.9, and 67.1 (C-1‴–5‴)]. In the heteronuclear multiple bond correlation (HMBC) spectrum of **1**, long-range correlations were observed between H-1″ of Rha (δ_H 6.48) and C-2′ of Ara (δ_C 72.8), H-1‴ of Xyl (δ_H 4.94) and C-3′ of Ara (δ_C 85.2), between H-1′ of Ara (δ_H 4.69) and C-1 of the aglycone (δ_C 84.0). Furthermore, a $^3J_{C,H}$ correlation was observed between H-4″ of Rha (δ_H 5.78) and the acetyl carbonyl carbon (δ_C 170.8). Accordingly, **1** was determined to be (23*S*,24*S*,25*S*)-3β,23,24-trihydroxyspirost-5-en-1β-yl *O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **2** ($C_{51}H_{80}O_{23}$) indicated that **2** was analogous to **1**, including the triglycoside moiety attached to C-1 of the aglycone. However, the molecular formula of **2** was larger than that of **1** by a $C_6H_{10}O_4$ unit, indicating the presence of an additional hexosyl unit. Acid hydrolysis of **2** yielded L-arabinose, L-rhamnose, D-quinovose, and D-xylose, while ^{1}H-^{1}H COSY and HSQC analysis indicated that **2** contained a terminal β-D-quinovopyranosyl unit [Qui: δ_H 5.24 (1H, d, $J = 7.6$ Hz, H-1⁗); δ_C 105.3, 76.2, 78.1, 76.9, 73.0, and 18.6 (C-1⁗–6⁗)]. Comparing the ^{13}C-NMR spectrum of **2** with that of **1**, the signal attributed to C-24 of the aglycone was shifted downfield by 8.4 ppm. Additionally, the HMBC spectrum of **2** showed a long-range correlation between H-1⁗ of Qui (δ_H 5.24) and C-24 of the aglycone (δ_C 81.4). Therefore, **2** was determined to be (23*S*,24*S*,25*S*)-24-[(β-D-quinovopyranosyl)-oxy]-3β,23-dihydroxyspirost-5-en-1β-yl *O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** ($C_{50}H_{78}O_{23}$) with those of **1** suggested that **3** contained the same aglycone moiety as **1** but differed in terms of the sugar moiety attached to C-1 of the aglycone. Acid hydrolysis of **3** afforded L-arabinose, D-apiose, L-rhamnose, and D-xylose, while ^{1}H-^{1}H COSY and HSQC analysis of the sugar moiety in **3** showed that it consisted of a 2,3-disubstituted α-L-arabinopyranosyl (Ara), 3,4-disubstituted α-L-rhamnopyranosyl (Rha), terminal β-D-xylopyranosyl (Xyl), and terminal β-D-apiofuranosyl units [Api: δ_H 5.95 (1H, brs, H-1⁗); δ_C 112.1, 77.8, 80.0, 74.8, and 65.2 (C-1⁗–5⁗)], as well as an acetyl group. The α-anomeric

configuration of Rha was determined by the large $^{1}J_{C\text{-}1,H\text{-}1}$ value of 169.7 Hz. In the HMBC spectrum of **3**, long-range correlations were observed between H-1‴′ of Api (δ_H 5.95) and C-3″ of Rha (δ_C 77.7), H-1″ of Rha (δ_H 6.49) and C-2′ of Ara (δ_C 72.4), H-1‴ of Xyl (δ_H 4.92) and C-3′ of Ara (δ_C 85.2), H-4″ of Rha (δ_H 5.90) and the acetyl carbonyl carbon (δ_C 170.7), and between H-1′ of Ara (δ_H 4.63) and C-1 of the aglycone (δ_C 84.2). Thus, **3** was determined to be (23*S*,24*S*,25*S*)-3*β*,23,24-trihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

Compound **4** ($C_{56}H_{88}O_{27}$) exhibited ^{1}H- and ^{13}C-NMR spectral features similar to those of **3**, except for the signals arising from the F-ring part of the steroidal skeleton. The molecular formula of **4** featured an additional $C_6H_{10}O_4$ compared to that of **3**. From acid hydrolysis of **4**, L-arabinose, D-apiose, D-fucose, L-rhamnose, and D-xylose were obtained. A terminal *β*-D-fucopyranosyl unit [Fuc: δ_H 5.13 (1H, d, J = 7.9 Hz, H-1⁗); δ_C 105.8, 73.1, 75.1, 72.6, 71.3, and 17.1 (C-1⁗–6⁗)] was detected by ^{1}H-^{1}H COSY and HSQC spectral analysis of **4**. Comparing the ^{13}C-NMR spectrum of **4** with that of **3**, the signal assigned to C-24 of the aglycone was shifted downfield by 8.4 ppm and a $^{3}J_{C,H}$ correlation was observed between H-1⁗ of Fuc (δ_H 5.13) and C-24 of the aglycone (δ_C 81.4) in the HMBC spectrum. Therefore, **4** was elucidated as (23*S*,24*S*,25*S*)-24-[(*β*-D-fucopyranosyl)-oxy]-3*β*,23-dihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **5** ($C_{49}H_{78}O_{23}$) were essentially analogous to those of **22**, but remarkable differences were observed for the signals assigned to the monosaccharide linked to C-24 of the aglycone between the two glycosides. Acid hydrolysis of **5** yielded L-arabinose, D-glucose, L-rhamnose, and D-xylose. Analysis of the associated ^{1}H-^{1}H COSY and HSQC spectra indicated the presence of a terminal *β*-D-glucopyranosyl unit [Glc: δ_H 5.33 (1H, d, J = 7.7 Hz, H-1⁗); δ_C 105.6, 76.1, 78.3, 69.5, 78.3, and 63.0 (C-1⁗–6⁗)]. The HMBC spectrum of **5** showed a long-range correlation between H-1⁗ of Glc (δ_H 5.33) and C-24 of the aglycone (δ_C 81.6). Accordingly, **5** was determined to be (23*S*,24*S*,25*S*)-24-[(*β*-D-glucopyranosyl)oxy]-3*β*,23-dihydroxyspirost-5-en-1*β*-yl *O*-*α*-L-rhamnopyranosyl-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **6** ($C_{45}H_{70}O_{20}$), **7** ($C_{51}H_{80}O_{24}$), and **8** ($C_{50}H_{78}O_{24}$) were closely related to those of **1**, **23**, and **3**, respectively. The molecular formula of **6** was larger than that of **1** ($C_{45}H_{70}O_{19}$) by a single oxygen atom, and only differences observed in the ^{1}H- and ^{13}C-NMR signals were those assigned to Me-21/C-21. The methyl signals [δ_H 1.13 (3H, d, J = 7.0 Hz); δ_C 14.6] in **1** were displaced by hydroxymethyl signals [δ_H 4.22 (1H, brd, J = 10.1 Hz) and 4.01 (1H, dd, J = 10.1, 6.7 Hz); δ_C 62.3] in **6**. Similarly, the molecular formulas of **7** and **8** were larger than those of **23** ($C_{51}H_{80}O_{23}$) and **3** ($C_{50}H_{78}O_{23}$) by a single oxygen atom, and the C-21 methyl groups were hydroxylated, as indicated by the ^{1}H- and ^{13}C-NMR spectra [**7**: δ_H 4.20 (1H, brd, J = 10.4 Hz) and 4.01 (1H, dd, J = 10.4, 7.1 Hz); δ_C 62.5; **8**: δ_H 4.19 (1H, m), 3.98 (1H, m); δ_C 62.3)]. Therefore, **6**, **7**, and **8** were identified as the corresponding C-21 hydroxy derivatives of **1**, **23**, and **3**, respectively, establishing them as (23*S*,24*S*,25*S*)-3*β*,21,23,24-tetrahydroxyspirost-5-en-1*β*-yl *O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, (23*S*,24*S*,25*S*)-24-[(*β*-D-fucopyranosyl)oxy]-3*β*,21,23-trihydroxyspirost-5-en-1*β*-yl *O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, and (23*S*,24*S*,25*S*)-3*β*,21,23,24-tetrahydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, respectively.

The ^{1}H- and ^{13}C-NMR spectra of **9** ($C_{55}H_{86}O_{28}$) were similar to those obtained for **8**, except for the presence of the signals attributed to one more monosaccharide unit. The molecular formula of **9** was larger than that of **8** by $C_5H_8O_4$, corresponding to a single pentosyl unit. Acid hydrolysis of **9** yielded L-arabinose, D-apiose, L-rhamnose, and D-xylose. Analysis of the corresponding ^{1}H-^{1}H COSY and HSQC spectra of the sugar moieties of **9** indicated the presence of an additional terminal *α*-L-arabinopyranosyl unit [Ara′: δ_H 5.11 (1H, d, J = 7.7 Hz, H-1⁗); δ_C 106.4, 73.6, 74.8, 69.9, and 67.2 (C-1⁗–5⁗)]. A long-range correlation was observed between H-1⁗ of Ara′ (δ_H 5.11) and C-24 of the aglycone (δ_C 81.7) in the HMBC spectrum. Thus, **9** was identified as (23*S*,24*S*,25*S*)-24-[(*β*-D-arabinopyranosyl)oxy]-3*β*,21,23-trihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

Analysis of the ^{1}H- and ^{13}C-NMR spectra of **10** ($C_{56}H_{88}O_{28}$) and subsequent comparison with those of **9** revealed that the aglycone and tetraglycoside attached to C-1 of the aglycone were identical to those of **9** but differed in terms of the monosaccharide linked to C-24 of the aglycone. Instead of the signals for an arabinopyranosyl moiety, signals attributed to a *β*-D-fucopyranosyl (Fuc) residue were observed. Acid hydrolysis of **10** yielded L-arabinose, D-apiose, D-fucose, L-rhamnose, and D-xylose. The linkage of the Fuc moiety to C-24 of the aglycone was confirmed by an HMBC correlation between H-1⁗ of Fuc (δ_H 5.13) and C-24 of the aglycone (δ_C 81.7). Thus, **10** was assigned as (23*S*,24*S*,25*S*)-24-[(*β*-D-fucopyranosyl)oxy]-3*β*,21,23-trihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **11** ($C_{56}H_{88}O_{29}$) suggested that it was analogous to **8**, including the tetraglycoside moiety attached to C-1 of the aglycone. The molecular formula of **11** was larger than that of **8** by $C_6H_{10}O_5$, corresponding to a single hexosyl unit. Acid hydrolysis of **11** yielded L-arabinose, D-apiose, D-galactose, L-rhamnose, and D-xylose. The ^{1}H-^{1}H COSY and HSQC spectral analysis of **11** indicated the presence of a terminal *β*-D-galactopyranosyl unit [Gal: δ_H 4.90 (1H, d, J = 7.9 Hz, H-1⁗); δ_C 105.4, 72.5, 75.6, 70.2, 77.0, and 62.4 (C-1⁗–6⁗)], and an HMBC correlation was observed between H-1⁗ of Gal (δ_H 4.90) and C-21 of the aglycone (δ_C 70.0). Therefore, **11** was determined to be (23*S*,24*S*,25*S*)-21-[(*β*-D-galactopyranosyl)oxy]-3*β*,23,24-trihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **12** ($C_{61}H_{96}O_{33}$) were similar to those obtained for **11**, but the molecular formula of **12** was larger than that of **11** by $C_5H_8O_4$. Acid hydrolysis of **12** afforded L-arabinose, D-apiose, D-galactose,

Table 1. ^{1}H-NMR Data for the Aglycone Moiety of **1**–**21**

1			**2**			**3**			**4**			**5**			**6**			**7**		
Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)
1	3.83 dd	12.0, 4.1	1	3.81 dd	12.0, 4.1	1	3.77 dd	11.9, 4.4	1	3.76 dd	11.6, 2.6	1	3.78 br d	11.2	1	3.82 dd	11.9, 3.5	1	3.80 dd	11.6, 3.5
2 a	2.72 br d	12.0	2 a	2.73 br d	12.0	2 a	2.72 br d	11.9	2 a	2.70 br d	11.6	2 a	2.73 br d	11.2	2 a	2.71 br d	11.9	2 a	2.71 br d	11.6
b	2.33 q-like	12.0	b	2.33 q-like	12.0	b	2.35 q-like	11.9	b	2.34 q-like	11.6	b	2.41 q-like	11.2	b	2.32 q-like	11.9	b	2.31 q-like	11.6
3	3.90 m	$W_{1/2}$ = 23.8	3	3.90 m	$W_{1/2}$ = 19.1	3	3.89 m	$W_{1/2}$ = 22.6	3	3.87 m	$W_{1/2}$ = 18.2	3	3.86 m	$W_{1/2}$ = 20.0	3	3.90 m	$W_{1/2}$ = 22.0	3	3.90 m	$W_{1/2}$ = 21.1
4 a	2.71 t-like	12.4	4 a	2.75 t-like	13.4	4 a	2.70 t-like	13.5	4 a	2.73 t-like	12.8	4 a	2.71 t-like	11.9	4 a	2.69 t-like	12.5	4 a	2.71 t-like	12.6
b	2.62 dd	12.4, 4.3	b	2.65 dd	13.4, 4.7	b	2.60 dd	13.5, 4.9	b	2.63 dd	12.8, 3.8	b	2.59 dd	11.9, 3.2	b	2.62 dd	12.5, 4.1	b	2.64 dd	12.6, 3.9
5	—		5	—		5	—		5	—		5	—		5	—		5	—	
6	5.60 br d	5.8	6	5.57 br d	5.7	6	5.59 br d	4.2	6	5.63 br d	5.3	6	5.57 br d	5.5	6	5.60 br d	5.2	6	5.62 br d	5.4
7 a	1.89 m		7 a	1.79 m		7 a	1.89 m		7 a	1.75 m		7 a	1.74 m		7 a	1.88 m		7 a	1.75 m	
b	1.53 m		b	1.47 m		b	1.48 m		b	1.47 m		b	1.45 m		b	1.54 m		b	1.46 m	
8	1.57 m		8	1.50 m		8	1.59 m		8	1.55 m		8	1.46 m		8	1.58 m		8	1.49 m	
9	1.53 m		9	1.49 m		9	1.50 m		9	1.50 m		9	1.47 m		9	1.51 m		9	1.50 m	
10	—		10	—		10	—		10	—		10	—		10	—		10	—	
11 a	2.89 br d	10.1	11 a	2.87 br d	11.9	11 a	2.88 br d	10.0	11 a	2.86 br d	11.5	11 a	2.89 m		11 a	2.87 br d	11.5	11 a	2.85 br d	11.6
b	1.55 m		b	1.54 m		b	1.54 m		b	1.52 m		b	1.54 m		b	1.52 m		b	1.52 m	
12 a	1.56 m		12 a	1.53 m		12 a	1.57 m		12 a	1.52 m		12 a	1.51 m		12 a	1.79 m		12 a	1.75 m	
b	1.31 m		b	1.27 m		b	1.30 m		b	1.26 m		b	1.26 m		b	1.34 m		b	1.30 m	
13	—		13	—		13	—		13	—		13	—		13	—		13	—	
14	1.15 m		14	1.09 m		14	1.16 m		14	1.06 m		14	1.07 m		14	1.17 m		14	1.10 m	
15 a	1.96 m		15 a	1.87 m		15 a	1.96 m		15 a	1.81 m		15 a	1.85 m		15 a	2.02 m		15 a	1.86 m	
b	1.40 m		b	1.48 m		b	1.51 m		b	1.43 m		b	1.46 m		b	1.45 m		b	1.51 m	
16	4.61 m		16	4.61 m		16	4.60 m		16	4.58 m		16	4.19 m		16	4.68 m		16	4.66 m	
17	1.74 dd	8.0, 7.6	17	1.70 dd	8.8, 6.2	17	1.73 dd	7.9, 7.4	17	1.68 dd	7.4, 7.4	17	1.68 m		17	1.96 dd	8.2, 7.1	17	1.93 dd	7.4, 7.1
18	1.02 s		18	1.01 s		18	1.01 s		18	0.99 s		18	0.98 s		18	1.09 s		18	1.08 s	
19	1.35 s		19	1.38 s		19	1.34 s		19	1.37 s		19	1.41 s		19	1.33 s		19	1.36 s	
20	2.97 m		20	2.91 m		20	2.96 m		20	2.88 m		20	2.89 m		20	3.38 q-like	6.7	20	3.30 q-like	6.5
21	1.13 d	7.0	21	1.11 d	6.7	21	1.11 d	5.6	21	1.09 d	6.8	21	1.09 d	6.5	21 a	4.22 br d	10.1	21 a	4.20 br d	10.4
22	—		22	—		22	—		22	—		22	—		b	4.01 dd	10.1, 6.7	b	4.01 dd	10.4, 7.1
23	3.81 d	3.2	23	3.87 d	3.9	23	3.81 d	3.1	23	3.83 d	2.1	23	3.83 br s		22	—		22	—	
24	4.10 br s		24	4.18 br s		24	4.10 br s		24	4.17 br s		24	4.17 br s		23	4.30 d	3.3	23	4.35 d	2.6
25	1.89 m		25	1.94 m		25	1.88 m		25	1.91 m		25	1.89 m		24	4.09 br s		24	4.16 br s	
26 ax	3.82 dd	11.2, 11.2	26 ax	3.97 dd	11.2, 11.2	26 ax	3.82 dd	11.5, 11.5	26 ax	3.92 dd	10.6, 10.6	26 ax	3.96 dd	10.9, 10.9	25	1.91 m		25	1.98 m	
eq	3.43 dd	11.2, 4.7	eq	3.38 dd	11.2, 4.2	eq	3.43 dd	11.5, 4.4	eq	3.34 dd	10.6, 4.1	eq	3.35 dd	10.9, 3.7	26 ax	3.87 dd	11.0, 11.0	26 ax	3.97 dd	10.7, 10.7
27	0.97 d	6.8	27	1.08 d	6.7	27	0.96 d	6.7	27	1.05 d	6.7	27	1.03 d	6.3	eq	3.44 dd	11.0, 4.3	eq	3.37 dd	10.7, 4.4
															27	0.95 d	6.7	27	1.04 d	6.7

Table 1. Continued

8			9			10			11			12			13			14		
Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)
1	3.77 dd	11.9, 3.8	1	3.78 dd	11.8, 3.8	1	3.79 dd	11.8, 3.9	1	3.73 dd	11.8, 3.8	1	3.73 dd	11.8, 3.6	1	3.76 dd	11.4, 4.1	1	3.74 dd	11.8, 3.1
2 a	2.69 br d	11.9	2 a	2.70 br d	11.8	2 a	2.71 br d	11.8	2 a	2.68 br d	11.8	2 a	2.67 br d	11.8	2 a	2.72 br d	11.4	2 a	2.70 br d	11.8
b	2.33 q-like	11.9	b	2.34 q-like	11.8	b	2.35 q-like	11.8	b	2.35 q-like	11.8	b	2.35 q-like	11.8	b	2.37 q-like	11.4,	b	2.35 q-like	11.8
3	3.86 m	$W_{1/2}$ = 23.5	3	3.88 m	$W_{1/2}$ = 21.3	3	3.88 m	$W_{1/2}$ = 22.3	3	3.89 m	$W_{1/2}$ = 21.6	3	3.87 m	$W_{1/2}$ = 18.8	3	3.84 m	$W_{1/2}$ = 22.0	3	3.87 m	$W_{1/2}$ = 22.2
4 a	2.70 t-like	12.6	4 a	2.74 t-like	12.8	4 a	2.75 t-like	12.6	4 a	2.70 t-like	12.1	4 a	2.73 t-like	12.7	4 a	2.68 t-like	12.9	4 a	2.70 t-like	14.0
b	2.59 dd	12.6, 4.5	b	2.63 dd	12.8, 4.6	b	2.63 dd	12.6, 4.2	b	2.59 dd	12.1, 5.0	b	2.62 dd	12.7, 4.6	b	2.57 dd	12.9, 4.4	b	2.59 dd	14.0, 4.6
5	—		5	—		5	—		5	—		5	—		5	—		5	—	
6	5.59 br d	5.7	6	5.63 br d	5.5	6	5.63 br d	4.9	6	5.59 br d	5.7	6	5.61 br d	5.5	6	5.55 [1)]		6	5.56 [1)]	
7 a	1.88 m		7 a	1.77 m		7 a	1.75 m		7 a	1.88 m		7 a	1.77 m		7 a	1.69 m		7 a	1.87 m	
b	1.54 m		b	1.49 m		b	1.46 m		b	1.53 m		b	1.46 m		b	1.41 m		b	1.51 m	
8	1.58 m		8	1.50 m		8	1.48 m		8	1.54 m		8	1.48 m		8	1.40 m		8	1.49 m	
9	1.46 m		9	1.47 m		9	1.49 m		9	1.50 m		9	1.46 m		9	1.42 m		9	1.40 m	
10	—		10	—		10	—		10	—		10	—		10	—		10	—	
11 a	2.87 br d	10.5	11 a	2.85 br d	11.0	11 a	2.86 br d	10.9	11 a	2.82 br d	9.7	11 a	2.80 br d	9.3	11 a	2.79 br d	8.2	11 a	2.77 br d	10.9
b	1.51 m		b	1.53 dd	11.0, 5.8	b	1.52 m		b	1.47 m		b	1.44 m		b	1.38 m		b	1.40 m	
12 a	1.79 m		12 a	1.75 m		12 a	1.77 m		12 a	1.70 m		12 a	1.70 m		12 a	1.27 m		12 a	1.26 m	
b	1.33 m		b	1.31 m		b	1.32 m		b	1.33 m		b	1.30 m		b	1.10 m		b	1.11 m	
13	—		13	—		13	—		13	—		13	—		13	—		13	—	
14	1.17 m		14	1.12 m		14	1.12 m		14	1.12 m		14	1.10 m		14	1.01 m		14	1.06 m	
15 a	1.89 m		15 a	1.88 m		15 a	1.87 m		15 a	1.96 m		15 a	1.88 m		15 a	1.78 m		15 a	1.87 m	
b	1.43 m		b	1.55 m		b	1.50 m		b	1.43 m		b	1.53 m		b	1.43 m		b	1.51 m	
16	4.65 m		16	4.68 m		16	4.67 m		16	4.61 m		16	4.63 m		16	4.57 m		16	4.59 m	
17	1.96 m		17	1.93 dd	8.3, 6.3	17	1.94 dd	8.2, 6.4	17	1.84 dd	8.0, 7.4	17	1.85 dd	7.4, 7.4	17	1.66 dd	6.5, 6.5	17	1.66 dd	7.2, 7.2
18	1.09 s		18	1.08 s		18	1.09 s		18	1.06 s		18	1.06 s		18	0.98 s		18	0.99 s	
19	1.33 s		19	1.37 s		19	1.38 s		19	1.30 s		19	1.34 s		19	1.38 s		19	1.31 s	
20	3.35 q-like	6.6	20	3.31 q-like	6.8	20	3.32 q-like	6.7	20	3.46 q-like	6.9	20	3.38 q-like	6.9	20	3.36 q-like	8.2	20	3.43 q-like	7.4
21 a	4.19 m		21 a	4.20 br d	10.7	21 a	4.20 br d	10.4	21 a	4.51 m		21 a	4.50 m		21 a	4.57 m		21 a	4.57 m	
b	3.98 m		b	4.01 dd	10.7 6.8	b	4.02 dd	10.4, 6.7	b	3.89 m		b	3.83 m		b	3.81 m		b	3.76 m	
22	—		22	—		22	—		22	—		22	—		22	—		22	—	
23	4.27 d	3.6	23	4.35 d	3.2	23	4.36 d	3.2	23	4.22 d	3.4	23	4.29 d	2.8	23	4.44 d	3.4	23	4.37 d	2.8
24	4.02 br s		24	4.16 br s		24	4.17 br s		24	3.97 br s		24	4.03 br s		24	4.14 br s		24	4.00 br s	
25	1.91 m		25	1.97 m		25	1.99 m		25	1.82 m		25	1.89 m		25	1.96 m		25	1.85 m	
26 ax	3.84 dd	11.2, 11.2	26 ax	3.97 dd	11.3, 11.3	26 ax	3.99 dd	11.1, 11.1	26 ax	3.80 dd	11.5, 11.5	26 ax	3.92 dd	10.6, 10.6	26 ax	3.91 dd	11.6, 11.6	26 ax	3.77 dd	11.2, 11.2
eq	3.43 dd	11.2, 4.8	eq	3.36 dd	11.3, 4.5	eq	3.37 dd	11.1, 4.4	eq	3.39 dd	11.5, 4.6	eq	3.29 dd	10.6, 4.4	eq	3.28 dd	11.6, 5.0	eq	3.32 dd	11.2, 4.5
27	0.94 d	6.8	27	1.03 d	6.8	27	1.05 d	6.9	27	0.90 d	6.8	27	0.99 d	7.0	27	0.98 d	5.3	27	0.86 d	6.3

Table 1. Continued

15			16			17			18			19			20			21		
Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)
1	3.73 dd	11.9, 3.7	1	3.76 dd	11.8, 4.7	1	3.78 dd	11.8, 4.0	1	3.78 dd	11.9, 3.8	1	3.77 dd	12.0, 3.8	1	3.80 dd	11.8, 3.6	1	3.87 dd	11.5, 3.2
2 a	2.70 br d	11.9	2 a	2.72 br d	11.8	2 a	2.70 br d	11.8	2 a	2.71 br d	11.9	2 a	2.72 br d	12.0	2 a	2.70 br d	11.8	2 a	2.81 br d	11.5
b	2.35 q-like	11.9	b	2.35 q-like	11.8	b	2.34 q-like	11.8	b	2.34 q-like	11.9	b	2.35 q-like	12.0	b	2.33 q-like	11.8	b	2.12 q-like	11.5
3	3.86 m	$W_{1/2}$ = 21.0	3	3.88 m	$W_{1/2}$ = 20.5	3	3.90 m	$W_{1/2}$ = 20.6	3	3.89 m	$W_{1/2}$ = 22.3	3	3.89 m	$W_{1/2}$ = 28.1	3	3.89 m	$W_{1/2}$ = 20.6	3	3.91 m	$W_{1/2}$ = 23.4
4 a	2.72 t-like	13.2	4 a	2.73 t-like	12.1	4 a	2.73 t-like	11.7	4 a	2.72 t-like	12.3	4 a	2.73 t-like	12.4	4 a	2.73 t-like	12.8	4 a	2.66 br d	11.7
b	2.62 dd	13.2, 5.3	b	2.62 dd	12.1, 4.6	b	2.61 dd	11.7, 3.6	b	2.62 dd	12.3, 4.2	b	2.63 dd	12.4, 4.3	b	2.64 dd	12.8, 4.1	b	2.59 dd	11.7, 3.3
5	—		5	—		5	—		5	—		5	—		5	—		5	—	
6	5.60 br d	5.2	6	5.63 br d	5.5	6	5.59 br d	5.2	6	5.63 br d	6.3	6	5.65 br d	5.5	6	5.63 br d	5.4	6	5.55 br d	4.6
7 a	1.73 m		7 a	1.82 m		7 a	1.90 m		7 a	1.82 m		7 a	1.82 m		7 a	1.79 m		7 a	1.85 m	
b	1.45 m		b	1.51 m		b	1.56 m		b	1.50 m		b	1.51 m		b	1.50 m		b	1.49 m	
8	1.44 m		8	1.48 m		8	1.59 m		8	1.50 m		8	1.52 m		8	1.51 m		8	1.56 m	
9	1.41 m		9	1.50 m		9	1.51 m		9	1.50 m		9	1.52 m		9	1.49 m		9	1.46 m	
10	—		10	—		10	—		10	—		10	—		10	—		10	—	
11 a	2.76 br d	8.0	11 a	2.88 m		11 a	2.87 m		11 a	2.85 br d	10.6	11 a	2.94 br d	12.0	11 a	2.93 br d	12.7	11 a	2.91 br d	12.2
b	1.39 m		b	1.52 m		b	1.50 m		b	1.50 m		b	1.57 m		b	1.57 m		b	1.54 m	
12 a	1.28 m		12 a	1.78 m		12 a	1.79 m		12 a	1.76 m		12 a	1.79 m		12 a	1.76 m		12 a	1.64 m	
b	1.12 m		b	1.28 m		b	1.34 m		b	1.31 m		b	1.32 m		b	1.31 m		b	1.28 m	
13	—		13	—		13	—		13	—		13	—		13	—		13	—	
14	1.04 m		14	1.10 m		14	1.17 m		14	1.12 m		14	1.13 m		14	1.11 m		14	1.10 m	
15 a	1.80 m		15 a	1.79 m		15 a	2.00 m		15 a	1.89 m		15 a	1.89 m		15 a	1.87 m		15 a	1.98 m	
b	1.45 m		b	1.39 m		b	1.49 m		b	1.47 m		b	1.46 m		b	1.44 m		b	1.44 m	
16	4.59 m		16	4.58 m		16	4.70 m		16	4.67 m		16	4.65 m		16	4.64 m		16	4.92 m	
17	1.67 dd	7.6, 7.6	17	1.69 dd	8.6, 6.8	17	1.96 dd	8.5, 6.7	17	1.92 dd	8.5, 6.8	17	1.84 dd	8.4, 8.4	17	1.82 dd	8.1, 6.2	17	1.88 m	
18	1.00 s		18	0.94 s		18	1.10 s		18	1.01 s		18	1.03 s		18	1.03 s		18	0.90 s	
19	1.35 s		19	1.36 s		19	1.33 s		19	1.35 s		19	1.38 s		19	1.36 s		19	1.21 s	
20	3.36 m		20	2.87 m		20	3.40 q-like	6.5	20	3.31 m		20	3.25 m		20	3.25 q-like	6.5	20	2.18 m	
21 a	4.56 m		21	1.05 d	7.0	21 a	4.21 m		21 a	4.17 m		21 a	4.37 m		21 a	4.37 m		21	1.27 d	7.1
b	3.81 m		22	—		b	4.00 m		b	3.98 m		b	4.34 m		b	4.33 m		22	—	
22	—		23	3.96 d	4.1	22	—		22	—		22	—		22	—		23 a	2.01 m	
23	4.29 d	2.8	24	4.79 br d	4.1	23	4.44 d	4.0	23	4.48 d	4.0	23	4.14 d	4.0	23	4.14 d	4.0	b	1.65 m	
24	4.15 br s		25	—		24	4.68 br s		24	4.73 d	4.0	24	4.74 d	4.0	24	4.74 br s		24 a	2.00 m	
25	1.97 m		26 ax	4.81 d	12.4	25	—		25	—		25	—		25	—		b	1.64 m	
26 ax	3.91 dd	10.5, 10.5	eq	3.98 d	12.4	26 ax	4.88 d	12.4	26 ax	4.87 d	12.3	26 ax	4.82 d	12.0	26 ax	4.81 d	12.1	25	1.88 m	
eq	3.28 dd	10.5, 4.6	27 a	5.23 br s		eq	4.01 d	12.4	eq	3.99 d	12.3	eq	3.96 d	12.0	eq	3.96 d	12.1	26 ax	3.89 br d	9.0
27	0.97 d	6.6	b	5.08 br s		27 a	5.05 br s		27 a	5.20 br s		27 a	5.24 br s		27 a	5.24 br s		eq	3.59 br d	9.0
						b	4.95 br s		b	5.06 br s		b	5.11 br s		b	5.10 br s		27	0.95 d	6.5

All spectra were measured in C_5D_5N (**1**, **8**, **18**, and **19**: 500 MHz; **2-7**, **9-17**, **20**, and **21**: 600 MHz). 1) Signals are unclear due to overlapping with water signal.

Table 2. ^{13}C-NMR Data for the Aglycone Moiety of **1**–**21**

Positions	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
1	84.0	84.0	84.2	84.0	83.9	83.9	83.9	84.1	84.1	84.1	84.4	84.3	83.7	84.2	84.1	84.2	84.1	84.1	84.3	84.0	83.1
2	37.6	37.5	37.8	37.7	37.5	37.5	37.4	37.7	37.7	37.7	38.0	37.9	37.5	37.9	37.9	37.8	37.7	37.8	38.0	37.7	37.5
3	68.0	67.9	67.9	67.8	68.3	68.0	68.0	68.0	68.0	68.0	68.0	68.1	68.2	68.0	67.9	67.9	68.0	68.0	68.0	68.0	68.0
4	43.9	43.9	43.7	43.6	43.9	43.9	43.9	43.8	43.7	43.8	43.7	43.7	43.9	43.8	43.8	43.7	43.7	43.8	43.8	43.9	43.7
5	139.3	139.4	139.2	139.3	139.7	139.3	139.5	139.4	139.5	139.5	139.2	139.5	139.8	139.4	139.5	139.4	139.3	139.5	139.4	139.4	139.5
6	124.9	124.8	124.9	124.7	124.6	124.9	124.8	124.9	124.8	124.9	124.9	124.8	124.6	124.9	124.8	124.8	124.9	124.9	124.8	124.8	124.7
7	32.0	31.9	31.9	31.7	31.9	31.9	31.9	32.0	31.9	31.9	31.8	31.8	31.9	32.0	31.9	31.8	31.9	31.9	31.8	31.8	31.9
8	32.9	32.9	32.9	32.7	33.0	33.1	33.1	33.2	33.1	33.1	33.0	33.1	33.1	33.1	33.0	32.9	33.1	33.1	33.1	33.0	32.9
9	50.3	50.2	50.3	50.1	50.3	50.2	50.1	50.4	50.2	50.2	50.4	50.5	50.3	50.4	50.2	50.2	50.2	50.3	50.3	50.2	50.2
10	42.8	42.8	42.8	42.7	42.9	42.8	42.8	42.9	42.9	42.9	42.7	42.8	42.9	42.9	42.8	42.8	42.8	42.9	42.8	42.7	42.8
11	23.9	23.8	23.9	23.7	23.9	23.9	23.8	23.9	23.8	23.8	24.0	24.0	23.9	23.8	23.7	23.8	23.9	23.9	24.0	24.0	23.7
12	40.5	40.3	40.5	40.2	40.5	40.3	40.1	40.3	40.1	40.2	40.2	40.1	39.9	40.3	39.8	40.3	40.3	40.2	39.9	39.9	40.3
13	40.6	40.7	40.6	40.6	40.8	40.8	40.9	40.9	40.9	41.0	40.8	41.1	40.9	40.7	40.8	40.6	40.8	40.9	40.9	40.9	40.4
14	56.8	56.6	56.7	56.5	56.8	56.9	56.7	57.0	56.8	56.8	57.0	57.1	56.9	57.0	56.8	56.6	56.9	56.8	56.9	56.8	56.6
15	32.2	32.4	32.2	32.2	32.4	32.4	32.5	32.5	32.5	32.6	32.2	32.4	32.4	32.3	32.4	32.3	32.4	32.5	32.4	32.3	32.6
16	83.0	82.6	82.9	82.5	82.7	83.4	83.2	83.5	83.2	83.2	83.3	83.1	83.0	83.1	82.8	82.9	83.6	83.4	83.6	83.6	81.0
17	61.3	61.5	61.2	61.3	61.6	57.8	57.9	57.7	57.9	57.9	57.7	58.1	57.7	57.2	57.5	61.3	57.8	57.9	58.7	58.6	63.8
18	16.8	16.8	16.8	16.6	16.8	16.9	16.8	16.9	16.8	16.8	16.8	16.8	16.6	16.4	16.5	16.7	16.9	16.8	16.8	16.7	16.7
19	14.9	15.0	14.9	14.8	15.1	14.9	14.9	14.9	15.0	15.0	14.9	15.0	15.1	15.0	15.0	14.9	14.9	15.0	15.0	15.0	14.7
20	36.8	37.2	36.7	37.0	37.2	45.6	46.0	45.7	46.0	46.0	42.9	43.4	43.3	42.8	43.2	37.3	45.9	46.1	42.6	42.6	40.6
21	14.6	14.9	14.6	14.7	14.8	62.3	62.5	62.3	62.5	62.5	70.0	70.2	69.9	69.8	69.8	14.7	62.2	62.3	65.1	65.0	16.3
22	112.7	111.7	112.6	111.5	111.7	112.5	111.6	112.6	111.6	111.7	112.1	111.3	111.1	112.1	110.9	111.7	112.4	111.7	111.0	111.0	110.6
23	68.7	69.4	68.6	69.3	72.0	70.4	71.2	70.4	71.2	71.5	70.0	70.8	71.2	70.3	71.2	70.2	71.2	71.7	71.3	71.3	37.1
24	73.0	81.4	73.0	81.4	81.6	73.0	81.6	73.1	81.7	81.7	73.0	81.4	81.5	73.0	81.5	82.0	74.1	82.5	82.4	82.3	28.2
25	36.1	35.2	36.0	35.1	35.3	35.9	35.2	36.0	35.1	35.2	35.8	35.1	35.0	35.6	34.9	143.8	146.2	143.7	143.4	143.4	34.2
26	60.6	61.5	60.6	61.3	61.5	60.7	61.5	60.7	61.5	61.5	60.6	61.5	61.5	60.5	61.4	61.4	60.7	61.4	61.4	61.4	75.2
27	13.0	13.1	13.0	13.0	13.1	13.0	13.1	12.9	13.1	13.2	12.9	13.0	13.1	12.9	13.1	113.7	112.3	113.9	114.3	114.3	17.4

All spectra were measured in C_5D_5N (**1**, **8**, **18**, and **19**: 125 MHz; **2**–**7**, **9**–**17**, **20**, and **21**: 150 MHz).

Table 3. ^{1}H-NMR Data for the Sugar and Acetyl Moieties of **1**–**21**

1			**2**			**3**			**4**			**5**			**6**			**7**		
Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)	Positions	δ_H	*J* (Hz)
Ara 1'	4.69 d	7.9	Ara 1'	4.67 d	7.6	Ara 1'	4.63 d	7.6	Ara 1'	4.61 d	7.8	Ara 1'	4.68 d	7.5	Ara 1'	4.68 d	7.5	Ara 1'	4.66 d	7.4
2'	4.63 dd	8.5, 7.9	2'	4.61 dd	8.7, 7.6	2'	4.61 dd	8.8, 7.6	2'	4.58 dd	8.3, 7.8	2'	4.62 dd	8.8, 7.5	2'	4.61 dd	8.9, 7.5	2'	4.58 dd	8.8, 7.4
3'	4.09 dd	8.5, 3.7	3'	4.07 br d	8.7	3'	4.00 dd	8.8, 3.3	3'	3.99 dd	8.3, 2.2	3'	4.08 br d	8.8	3'	4.08 dd	8.9, 2.7	3'	4.05 dd	8.8, 2.9
4'	4.43 br s		4'	4.41 br s		4'	4.41 br s		4'	4.39 br s		4'	4.40 br s		4'	4.42 br s		4'	4.40 br s	
5' a	4.25 br d	10.1	5' a	4.23 br d	12.3	5' a	4.24 br d	10.6	5' a	4.26 br d	11.5	5' a	4.20 br d	11.3	5' a	4.23 br d	10.6	5' a	4.21 br d	11.8
b	3.69 br d	10.1	b	3.69 br d	12.3	b	3.65 br d	10.6	b	3.67 br d	11.5	b	3.66 br d	11.3	b	3.66 br d	10.6	b	3.66 br d	11.8
Rha 1''	6.48 br s		Rha 1''	6.47 br s		Rha 1''	6.49 br s		Rha 1''	6.48 br s		Rha 1''	6.33 br s		Rha 1''	6.48 br s		Rha 1''	6.45 br s	
2''	4.74 br s		2''	4.76 br s		2''	4.91 br s		2''	4.91 br s		2''	4.80 br s		2''	4.75 br s		2''	4.73 br s	
3''	4.69 br d	9.7	3''	4.70 dd	9.7, 2.6	3''	4.74 dd	9.5, 2.6	3''	4.73 dd	10.0, 2.3	3''	4.63 dd	9.5, 2.5	3''	4.69 br d	9.7	3''	4.67 dd	9.7, 2.8
4''	5.78 dd	9.7, 9.7	4''	5.77 dd	9.7, 9.7	4''	5.90 dd	9.5, 9.5	4''	5.88 dd	10.0, 10.0	4''	4.29 dd	9.5, 9.5	4''	5.77 dd	9.7, 9.7	4''	5.76 dd	9.7, 9.7
5''	4.91 m		5''	4.91 m		5''	4.93 m		5''	4.91 m		5''	4.82 m		5''	4.89 m		5''	4.88 m	
6''	1.43 d	6.1	6''	1.41 d	5.7	6''	1.41 d	6.0	6''	1.39 d	6.4	6''	1.69 d	5.2	6''	1.38 d	6.1	6''	1.35 d	6.6
Xyl 1'''	4.94 d	7.6	Xyl 1'''	4.94 d	7.9	Xyl 1'''	4.92 d	7.2	Xyl 1'''	4.93 d	7.1	Xyl 1'''	4.98 d	7.5	Xyl 1'''	4.95 d	7.6	Xyl 1'''	4.92 d	7.6
2'''	3.90 dd	8.3, 7.6	2'''	3.90 dd	7.9, 7.4	2'''	3.89 dd	8.0, 7.2	2'''	3.89 dd	7.9, 7.1	2'''	3.92 m		2'''	3.92 dd	8.4, 7.6	2'''	3.88 dd	8.6, 7.6
3'''	4.08 dd	8.7, 8.3	3'''	4.13 m		3'''	4.08 m		3'''	4.11 m		3'''	4.13 m		3'''	4.11 m		3'''	4.09 m	
4'''	4.10 m		4'''	4.11 m		4'''	4.10 m		4'''	4.12 m		4'''	4.12 m		4'''	4.12 m		4'''	4.10 m	
5''' a	4.28 dd	11.2, 3.8	5''' a	4.27 dd	10.6, 4.3	5''' a	4.26 dd	11.3, 4.2	5''' a	4.23 dd	12.1, 4.1	5''' a	4.28 br d	11.3	5''' a	4.30 br d	11.9	5''' a	4.26 dd	12.2, 4.3
b	3.67 dd	11.2, 7.3	b	3.66 br d	10.6	b	3.66 br d	11.3	b	3.72 dd	12.1, 6.2	b	3.67 br d	11.3	b	3.68 br d	11.9	b	3.70 dd	12.2, 6.7
Ac	2.01 s		Qui 1''''	5.24 d	7.6	Api 1''''	5.95 br s		Api 1''''	5.94 d	2.2	Glc 1''''	5.33 d	7.7	Ac	2.01 s		Fuc 1''''	5.11 d	7.8
			2''''	4.07 dd	8.6, 7.6	2''''	4.66 br s		2''''	4.65 d	2.2	2''''	4.08 dd	8.8, 7.7				2''''	4.43 dd	9.0, 7.8
			3''''	4.11 m		3''''	—		3''''	—		3''''	4.22 dd	8.8, 8.8				3''''	4.05 m	
			4''''	3.64 dd	10.4, 3.8	4'''' a	4.53 d	9.5	4'''' a	4.52 d	9.4	4''''	3.83 m					4''''	3.95 br d	2.8
			5''''	3.68 m		b	4.24 d	9.5	b	4.22 d	9.4	5''''	3.87 m					5''''	3.69 m	
			6''''	1.58 d	5.2	5'''' a	4.04 br s		5'''' a	4.03 br s		6'''' a	4.48 dd	11.4, 4.9				6''''	1.49 d	6.2
						b	4.04 br s		b	4.03 br s		b	4.35 br d	11.4						
			Ac	2.03 s														Ac	2.01 s	
						Ac	2.23 s		Fuc 1'''''	5.13 d	7.9									
									2'''''	4.43 dd	8.9, 7.9									
									3'''''	4.06 m										
									4'''''	3.96 br d	2.5									
									5'''''	3.72 m										
									6'''''	1.51 d	6.4									
									Ac	2.23 s										

Table 3. Continued

8			9			10			11			12			13			14		
Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)
Ara 1'	4.63 d	7.6	Ara 1'	4.62 d	7.7	Ara 1'	4.63 d	7.7	Ara 1'	4.61 d	7.4	Ara 1'	4.60 d	6.5	Ara 1'	4.67 d	7.1	Ara 1'	4.61 d	6.7
2'	4.57 dd	8.8, 7.6	2'	4.56 dd	8.9, 7.7	2'	4.57 dd	9.6, 7.7	2'	4.54 dd	9.1, 7.4	2'	4.46 dd	9.3, 6.5	2'	4.63 dd	10.3, 7.1	2'	4.60 dd	9.2, 6.7
3'	4.01 dd	8.8, 3.2	3'	3.99 dd	8.9, 2.4	3'	4.01 dd	9.6, 3.7	3'	4.01 dd	9.1, 3.2	3'	3.99 dd	9.3, 3.1	3'	4.07 dd	10.3, 2.9	3'	4.02 dd	9.2, 3.9
4'	4.41 br s		4'	4.39 br s		4'	4.41 br s		4'	4.41 br s		4'	4.38 br s		4'	4.42 br s		4'	4.42 br s	
5' a	4.27 br d	10.5	5' a	4.23 br d	11.5	5' a	4.21 br d	11.2	5' a	4.27 br d	11.1	5' a	4.27 m		5' a	4.29 br d	11.5	5' a	4.28 dd	11.6, 2.9
b	3.66 br d	10.5	b	3.65 br d	11.5	b	3.65 br d	11.2	b	3.68 br d	11.1	b	3.66 br d	10.7	b	3.67 br d	11.5	b	3.67 br d	11.6
Rha 1''	6.47 br s		Rha 1''	6.47 br s		Rha 1''	6.49 br s		Rha 1''	6.44 br s		Rha 1''	6.41 br s		Rha 1''	6.33 br s		Rha 1''	6.50 br s	
2''	4.90 br d	3.0	2''	4.90 br d	3.0	2''	4.92 br d	3.0	2''	4.92 br s		2''	4.91 br d	2.8	2''	4.80 br d	2.8	2''	4.93 br d	2.3
3''	4.72 dd	9.8, 3.0	3''	4.72 dd	9.8, 3.0	3''	4.73 dd	9.8, 3.0	3''	4.73 dd	9.8, 3.0	3''	4.72 dd	9.7, 2.8	3''	4.61 dd	8.9, 2.8	3''	4.75 dd	9.8, 2.3
4''	5.90 dd	9.8, 9.8	4''	5.89 dd	9.8, 9.8	4''	5.90 dd	9.8, 9.8	4''	5.90 dd	9.8, 9.8	4''	5.88 dd	9.7, 9.7	4''	4.29 dd	8.9, 8.9	4''	5.91 dd	9.8, 9.8
5''	4.88 m		5''	4.91 m		5''	4.90 m		5''	4.91 m		5''	4.90 m		5''	4.79 m		5''	4.94 m	
6''	1.37 d	6.1	6''	1.35 d	6.2	6''	1.36 d	6.2	6''	1.41 d	6.1	6''	1.39 d	5.4	6''	1.73 d	5.7	6''	1.44 d	5.7
Xyl 1'''	4.92 d	7.4	Xyl 1'''	4.90 d	7.3	Xyl 1'''	4.92 d	7.4	Xyl 1'''	4.91 d	7.7	Xyl 1'''	4.91 d	7.3	Xyl 1'''	4.98 d	7.4	Xyl 1'''	4.93 d	7.5
2'''	3.89 dd	8.2, 7.4	2'''	3.88 dd	8.9, 7.3	2'''	3.90 dd	8.7, 7.4	2'''	3.89 dd	8.8, 7.7	2'''	3.88 dd	8.5, 7.3	2'''	3.94 dd	8.0, 7.4	2'''	3.92 dd	8.8, 7.5
3'''	4.10 m		3'''	4.10 m		3'''	4.11 m		3'''	4.11 m		3'''	4.11 m		3'''	4.27 m		3'''	4.13 m	
4'''	4.11 m		4'''	4.11 m		4'''	4.11 m		4'''	4.11 m		4'''	4.10 m		4'''	4.12 m		4'''	4.12 m	
5''' a	4.27 br d	10.6	5''' a	4.26 dd	11.2, 4.3	5''' a	4.27 dd	11.4, 4.2	5''' a	4.29 dd	11.3, 4.2	5''' a	4.27 m		5''' a	4.29 m		5''' a	4.25 br d	12.4
b	3.67 br d	10.6	b	3.67 br d	11.2	b	3.68 br d	11.4	b	3.66 dd	11.3, 6.5	b	3.65 br d	12.5	b	3.68 br d	10.7	b	3.64 br d	12.4
Api 1''''	5.93 d	2.9	Api 1''''	5.94 d	3.1	Api 1''''	5.95 d	2.9	Api 1''''	5.95 d	2.9	Api 1''''	5.94 d	3.1	Gal 1''''	4.98 d	7.4	Api 1''''	5.96 d	3.2
2''''	4.66 br s		2''''	4.66 d	3.1	2''''	4.67 d	2.9	2''''	4.67 d	2.9	2''''	4.66 d	3.1	2''''	4.71 dd	8.8, 7.4	2''''	4.68 d	3.2
3''''	—		3''''	—		3''''	—		3''''	—		3''''	—		3''''	4.30 dd	8.8, 3.2	3''''	—	
4'''' a	4.51 d	9.3	4'''' a	4.52 d	9.4	4'''' a	4.53 d	9.4	4'''' a	4.54 d	9.3	4'''' a	4.54 d	9.6	4''''	4.55 br s		4'''' a	4.55 d	10.4
b	4.24 d	9.3	b	4.23 d	9.4	b	4.24 d	9.4	b	4.24 d	9.3	b	4.24 d	9.6	5''''	4.12 m		b	4.24 d	10.4
5'''' a	4.03 br s		5'''' a	4.03 br s		5'''' a	4.04 br s		5'''' a	4.05 br s		5'''' a	4.04 br s		6'''' a	4.44 m		5'''' a	4.06 br s	
b	4.03 br s		b	4.03 br s		b	4.04 br s		b	4.05 br s		b	4.04 br s		b	4.42 m		b	4.06 br s	
Ac	2.21 s		Ara' 1''''	5.11 d	7.7	Fuc 1''''	5.13 d	7.9	Gal 1''''	4.90 d	7.9	Gal 1''''	4.88 d	7.1	Glc 1''''	5.40 d	7.6	Gal 1''''	4.98 d	7.3
			2''''	4.52 m		2''''	4.44 dd	9.5, 7.9	2''''	4.47 dd	9.4, 7.9	2''''	4.46 dd	8.2, 7.1	2''''	4.15 dd	8.6, 7.6	2''''	4.70 dd	8.4, 7.3
			3''''	4.10 m		3''''	4.06 dd	9.5, 3.4	3''''	4.17 dd	9.4, 3.3	3''''	4.16 m		3''''	4.27 dd	8.6, 8.6	3''''	4.32 dd	8.4, 4.1
			4''''	4.18 br s		4''''	3.96 br d	3.4	4''''	4.56 br s		4''''	4.56 br s		4''''	4.28 dd	8.6, 8.6	4''''	4.56 br s	
			5'''' a	4.23 br d	11.4	5''''	3.71 m		5''''	4.11 m		5''''	4.09 m		5''''	4.01 m		5''''	4.13 m	
			b	3.65 br d	11.4	6''''	1.50 d	6.4	6'''' a	4.46 m		6'''' a	4.44 m		6'''' a	4.62 m		6'''' a	4.46 m	
									b	4.44 m		b	4.43 m		b	4.47 m		b	4.42 m	
			Ac	2.21 s		Ac	2.21 s													
									Ac	2.22 s		Ara' 1'''''	5.10 d	7.4	Fuc 1'''''	5.07 d	7.7	Glc 1'''''	5.38 d	7.4
												2'''''	4.51 dd	8.1, 7.4	2'''''	4.38 dd	8.6, 7.7	2'''''	4.13 dd	10.0, 7.4
												3'''''	4.09 dd	8.1, 4.3	3'''''	3.98 dd	8.6, 2.6	3'''''	4.26 dd	10.0, 10.0
												4'''''	4.17 br s		4'''''	3.90 br d	2.6	4'''''	4.34 dd	10.0, 10.0
												5''''' a	4.24 m		5'''''	3.63 m		5'''''	4.06 m	
												b	3.66 m		6'''''	1.47 d	6.1	6''''' a	4.63 br d	11.0
																		b	4.49 br d	11.0
												Ac	2.23 s							
																		Ac	2.24 s	

Table 3. Continued

15			16			17			18			19			20			21		
Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)	Positions	δ_H	J (Hz)
Ara 1'	4.60 d	7.4	Ara 1'	4.61 d	7.7	Ara 1'	4.62 d	7.7	Ara 1'	4.63 d	7.6	Ara 1'	4.63 d	7.5	Ara 1'	4.66 d	7.9	Ara 1'	4.75 d	7.1
2'	4.57 dd	8.8, 7.4	2'	4.57 dd	9.2, 7.7	2'	4.57 dd	9.1, 7.7	2'	4.56 dd	9.1, 7.6	2'	4.56 dd	9.2, 7.5	2'	4.57 dd	9.4, 7.9	2'	4.41 dd	8.8, 7.1
3'	3.99 dd	8.8, 3.0	3'	4.00 dd	9.2, 3.2	3'	4.01 dd	9.1, 3.5	3'	4.01 dd	9.1, 3.2	3'	4.01 dd	9.2, 3.1	3'	4.05 dd	9.4, 2.6	3'	4.13 dd	8.8, 2.5
4'	4.41 br s		4'	4.39 br s		4'	4.40 br s		4'	4.40 br s		4'	4.40 br s		4'	4.41 br s		4'	4.27 br s	
5' a	4.28 dd	10.7, 2.3	5' a	4.25 br d	11.0	5' a	4.24 br d	11.5	5' a	4.22 br d	11.7	5' a	4.23 dd	10.7, 1.7	5' a	4.22 br s	10.4	5' a	4.31 br d	12.1
b	3.66 br d	10.7	b	3.64 br d	11.0	b	3.65 br d	11.5	b	3.65 br d	11.7	b	3.66 br d	10.7	b	3.65 br d	10.4	b	3.71 br d	12.1
Rha 1''	6.50 br s		Rha 1''	6.48 br s		Rha 1''	6.48 d	1.3	Rha 1''	6.47 br s		Rha 1''	6.44 br s		Rha 1''	6.43 br s		Glc 1''	4.79 d	7.7
2''	4.93 br d	2.8	2''	4.91 br d	3.1	2''	4.92 br d	3.1	2''	4.91 br s		2''	4.90 br d	3.0	2''	4.74 br d	2.8	2''	4.01 dd	8.0, 7.7
3''	4.72 dd	9.9, 2.8	3''	4.73 dd	9.9, 3.1	3''	4.73 dd	9.8, 3.1	3''	4.72 dd	9.8, 3.3	3''	4.72 dd	9.8, 3.0	3''	4.68 dd	9.8, 2.8	3''	4.25 dd	8.8, 8.0
4''	5.90 dd	9.9, 9.9	4''	5.90 dd	9.9, 9.9	4''	5.89 dd	9.8, 9.8	4''	5.90 dd	9.8, 9.8	4''	5.89 dd	9.8, 9.8	4''	5.76 dd	9.8, 9.8	4''	4.24 dd	8.8, 8.8
5''	4.93 m		5''	4.92 m		5''	4.91 m		5''	4.98 m		5''	4.90 m		5''	4.89 m		5''	3.91 m	
6''	1.43 d	6.1	6''	1.39 d	6.1	6''	1.36 d	6.2	6''	1.36 d	5.7	6''	1.38 d	6.2	6''	1.38 d	5.8	6'' a	4.53 br d	11.4
																		b	4.37 dd	11.4, 5.8
Xyl 1'''	4.92 d	7.6	Xyl 1'''	4.91 d	7.6	Xyl 1'''	4.92 d	7.3	Xyl 1'''	4.91 d	7.7	Xyl 1'''	4.91 d	7.8	Xyl 1'''	4.93 d	7.6			
2'''	3.90 dd	8.0, 7.6	2'''	3.88 dd	8.6, 7.6	2'''	3.90 dd	8.2, 7.3	2'''	3.89 dd	8.4, 7.7	2'''	3.87 dd	8.5, 7.8	2'''	3.89 dd	8.5, 7.6			
3'''	4.12 m		3'''	4.11 m		3'''	4.12 m		3'''	4.09 m		3'''	4.07 m		3'''	4.09 m				
4'''	4.12 m		4'''	4.10 m		4'''	4.11 m		4'''	4.09 m		4'''	4.07 m		4'''	4.10 m				
5''' a	4.28 br d	11.4	5''' a	4.26 dd	12.4, 4.4	5''' a	4.27 dd	11.3, 4.7	5''' a	4.27 dd	11.7, 4.5	5''' a	4.23 dd	11.1, 3.9	5''' a	4.25 dd	11.3, 3.8			
b	3.66 br d	11.4	b	3.67 br d	12.4	b	3.67 br d	11.3	b	3.67 br d	11.7	b	3.67 dd	11.1, 8.2	b	3.66 br d	11.3			
Api 1''''	5.95 d	2.9	Api 1''''	5.95 d	3.2	Api 1''''	5.95 d	3.0	Api 1''''	5.93 d	2.9	Api 1''''	5.93 d	2.0	Ara' 1''''	5.16 d	6.7			
2''''	4.67 d	2.9	2''''	4.66 d	3.2	2''''	4.67 d	3.0	2''''	4.66 d	2.9	2''''	4.66 d	2.0	2''''	4.54 dd	8.5, 6.7			
3''''	—		3''''	—		3''''	—		3''''	—		3''''	—		3''''	4.18 dd	8.5, 3.1			
4'''' a	4.54 d	9.4	4'''' a	4.53 br d	9.4	4'''' a	4.54 br d	9.4	4'''' a	4.51 d	9.4	4'''' a	4.51 d	9.4	4''''	4.28 br s				
b	4.24 d	9.4	b	4.23 br d	9.4	b	4.24 br d	9.4	b	4.23 d	9.4	b	4.23 d	9.4	5'''' a	4.22 br d	12.1			
5'''' a	4.05 br s		5'''' a	4.04 br s		5'''' a	4.05 br s		5'''' a	4.03 br s		5'''' a	4.02 br s		b	3.74 br d	12.1			
b	4.05 br s		b	4.04 br s		b	4.05 br s		b	4.03 br s		b	4.02 br s							
															Ac (-C-21)	1.92 s				
Gal 1'''''	4.97 d	7.6	Fuc 1'''''	5.15 d	8.0	Ac	2.21 s		Ara' 1'''''	5.18 d	6.8	Ara' 1'''''	5.16 d	6.8	Ac' (-C-4'')	2.02 s				
2'''''	4.71 dd	9.5, 7.6	2'''''	4.41 dd	9.5, 8.0				2'''''	4.55 dd	8.4, 6.8	2'''''	4.54 dd	8.4, 6.8						
3'''''	4.30 dd	9.5, 3.4	3'''''	4.07 dd	9.5, 3.4				3'''''	4.17 dd	8.4, 4.5	3'''''	4.17 dd	8.4, 3.4						
4'''''	4.56 br s		4'''''	3.97 br d	3.4				4'''''	4.28 br s		4'''''	4.28 br s							
5'''''	4.11 m		5'''''	3.73 m					5''''' a	4.23 br d	10.8	5''''' a	4.23 br d	11.2						
6''''' a	4.45 m		6'''''	1.46 d	6.4				b	3.73 br d	10.8	b	3.75 br d	11.2						
b	4.42 m																			
			Ac	2.23 s					Ac	2.20 s		Ac (-C-21)	1.92 s							
Glc 1'''''	5.38 d	7.7										Ac' (-C-4'')	2.21 s							
2'''''	4.12 dd	9.5, 7.7																		
3'''''	4.26 dd	9.5, 9.5																		
4'''''	4.46 dd	9.5, 9.5																		
5'''''	4.00 m																			
6''''' a	4.62 dd	10.5, 2.3																		
b	4.47 m																			
Fuc 1''''''	5.08 d	7.8																		
2''''''	4.37 dd	9.1, 7.8																		
3''''''	3.99 dd	9.1, 3.7																		
4''''''	3.90 br d	3.7																		
5''''''	3.62 m																			
6''''''	1.46 d	6.4																		
Ac	2.23 s																			

All spectra were measured in C_5D_5N (**1**, **8**, **18**, and **19**: 500 MHz; **2**–**7**, **9**–**17**, **20**, and **21**: 600 MHz).

Table 4. ^{13}C-NMR Data for the Sugar and Acetyl Moieties of **1**–**21**

Positions	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara	Ara
1'	100.8	100.7	100.8	100.6	100.6	100.7	100.6	100.7	100.7	100.7	100.8	100.8	100.4	100.8	100.8	100.7	100.7	100.7	100.8	100.7	102.2
2'	72.8	72.6	72.4	72.2	73.9	72.6	72.6	72.6	72.4	72.5	72.7	72.3	74.3	72.8	72.6	72.4	72.4	72.5	72.6	72.8	72.6
3'	85.2	85.2	85.2	85.1	84.6	85.2	85.1	85.2	85.2	85.2	84.9	84.7	84.2	85.0	85.0	85.2	85.2	85.2	85.1	85.1	74.7
4'	69.9	69.8	69.7	69.5	69.5	69.9	69.8	69.7	69.7	69.8	69.6	69.5	69.9	69.7	69.8	69.7	69.7	69.7	69.6	69.7	69.6
5'	67.3	67.3	67.2	66.9	66.9	67.3	67.3	67.1	67.6	67.2	66.9	67.5	66.9	67.0	67.0	67.1	67.2	67.2	67.1	67.2	67.5
	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Glc
1"	100.7	100.8	100.5	100.4	101.7	100.8	100.7	100.6	100.5	100.6	100.7	100.7	101.9	100.8	100.7	100.5	100.5	100.6	100.6	100.8	104.8
2"	72.2	72.1	71.5	71.3	72.4	72.2	72.1	71.6	71.5	71.5	71.5	71.5	72.5	71.5	71.4	71.5	71.5	71.5	71.6	72.2	75.1
3"	69.9	69.8	77.7	77.5	72.5	69.9	69.8	77.8	77.7	77.7	77.7	77.7	72.4	77.7	77.7	77.7	77.7	77.7	77.8	69.9	78.5
4"	76.5	76.4	74.5	74.3	74.3	76.4	76.4	74.5	74.5	74.5	74.5	74.5	74.3	74.6	74.6	74.5	74.5	74.5	74.5	76.4	71.6
5"	66.5	66.4	66.6	66.4	69.5	66.4	66.4	66.7	66.6	66.6	66.7	67.0	69.6	66.8	66.7	66.6	66.6	66.6	66.6	66.4	78.4
6"	18.5	18.4	18.3	18.2	19.1	18.4	18.4	18.3	18.3	18.3	18.4	18.4	19.2	18.5	18.4	18.3	18.3	18.3	18.3	18.4	62.7
	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	Xyl	
1"'	106.7	106.6	106.7	106.5	106.3	106.7	106.3	106.6	106.6	106.7	106.6	106.4	106.4	106.6	106.7	106.6	106.7	106.7	106.7	106.7	
2"'	74.5	74.5	74.5	74.3	74.6	74.6	74.5	74.5	74.5	74.5	74.5	74.5	74.6	74.6	74.5	74.5	74.5	74.5	74.5	74.5	
3"'	78.5	78.4	78.4	78.3	78.2	78.5	78.4	78.4	78.4	78.5	78.5	78.4	78.2	78.4	78.4	78.4	78.4	78.5	78.5	78.5	
4"'	70.9	70.9	70.9	70.8	71.0	70.9	70.9	70.9	70.9	70.9	70.9	70.9	71.0	71.0	70.9	70.9	70.9	70.9	70.9	70.9	
5"'	67.1	67.0	67.0	67.0	67.0	67.1	67.0	67.1	67.0	67.1	67.1	67.5	67.0	67.0	67.1	67.0	67.0	67.1	67.1	67.1	
	Ac	Qui	Api	Api	Glc	Ac	Fuc	Api	Api	Api	Api	Api	Gal	Api	Api	Api	Api	Api	Api	Ara'	
1""	170.8	105.3	112.1	111.9	105.6	170.8	106.0	112.1	112.1	112.1	112.1	112.1	103.4	112.0	112.1	112.1	112.1	112.2	112.2	106.3	
2""	21.0	76.2	77.8	77.7	76.1	21.0	73.3	77.9	77.8	77.9	77.9	77.9	81.6	77.9	77.9	77.8	77.9	77.9	77.9	72.8	
3""		78.1	80.0	79.8	78.3		75.3	79.9	80.0	80.0	80.0	80.0	75.2	80.0	80.0	80.0	80.0	79.9	79.9	74.5	
4""		76.9	74.8	74.7	69.5		72.8	74.9	74.9	75.0	74.9	75.0	69.7	75.0	74.9	74.8	74.9	74.9	74.9	69.2	
5""		73.0	65.2	65.0	78.3		71.4	65.4	65.2	65.3	65.2	65.4	77.0	65.4	65.2	65.2	65.2	65.3	65.3	66.7	
6""		18.6			63.0		17.2						62.2								
		Ac	Ac	Fuc			Ac	Ac	Ara'	Fuc	Gal	Gal	Glc	Gal	Gal	Fuc	Ac	Ara'	Ara'	Ac (-C-21)	
1"""		170.8	170.7	105.8			170.7	170.6	106.4	106.0	105.4	105.3	106.1	103.5	103.5	106.2	170.7	106.1	106.3	170.8	
2"""		21.0	21.1	73.1			21.0	21.0	73.6	73.4	72.5	72.3	76.5	81.6	81.8	73.0	21.1	72.8	72.9	20.9	
3"""				75.1					74.8	75.4	75.6	74.6	78.1	75.2	75.3	75.3		74.5	74.5		
4"""				72.6					69.9	72.8	70.2	70.2	71.4	69.7	69.7	72.7		69.1	69.2		
5"""				71.3					67.2	71.2	77.0	76.9	78.6	77.0	77.0	71.5		66.5	66.6		
6"""				17.1						17.3	62.4	62.4	62.5	62.2	62.1	17.2					
				Ac					Ac	Ac	Ac	Ara'	Fuc	Glc	Glc	Ac		Ac	Ac (-C-21)	Ac' (-C-4")	
1""""				170.5					170.6	170.6	170.6	106.2	105.9	106.1	106.3	170.7		170.6	170.8	170.7	
2""""				20.9					21.1	21.1	21.1	73.0	73.4	76.7	76.7	21.1		21.1	20.9	21.0	
3""""												74.7	75.3	78.2	78.1						
4""""												69.9	72.8	71.3	71.1						
5""""												66.7	71.5	78.5	78.6						
6""""													17.2	62.2	62.2						
												Ac		Ac	Fuc						
1"""""												170.6		170.6	105.8				Ac' (-C-4")		
2"""""												21.1		21.1	73.3				170.6		
3"""""															75.2				21.1		
4"""""															72.8						
5"""""															71.5						
6"""""															17.2						
															Ac						
1""""""															170.7						
2""""""															21.1						

All spectra were measured in C_5D_5N (**1**, **8**, **18**, and **19**: 125 MHz; **2**–**7**, **9**–**17**, **20**, and **21**: 150 MHz).

L-rhamnose, and D-xylose. The ^{1}H-^{1}H COSY and HSQC spectral analysis of **12** indicated the presence of signals corresponding to an additional terminal α-L-arabinopyranosyl (Ara′) unit. The HMBC spectrum of **12** contained a long-range correlation from H-1"""" of Ara′ (δ_H 5.10) to C-24 of the aglycone (δ_C 81.4). Thus, **12** was assigned as (23*S*,24*S*,25*S*)-24-[(β-D-arabinopyranosyl)oxy]-21-[(β-D-galactopyranosyl)oxy]-3β,23-dihydroxyspirost-5-en-1β-yl *O*-β-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Compound **13** ($C_{61}H_{98}O_{33}$) was obtained as an amorphous powder and its ^{1}H- and ^{13}C-NMR spectra showed the same aglycone unit as **7**, also indicating that the sugar moieties attached to C-1 and C-24 of the aglycone of **13** were coincident with those of **22**. Additionally, a 2-substituted β-D-galactopyranosyl unit [Gal: δ_H 4.98 (1H, d, J = 7.4 Hz, H-1""); δ_C 103.4, 81.6, 75.2, 69.7, 77.0, and 62.2 (C-1""–6"")] and a terminal β-D-glucopyranosyl unit [Glc: δ_H 5.40 (1H, d, J = 7.6 Hz,

H-1‴″); δ_C 106.1, 76.5, 78.1, 71.4, 78.6, and 62.5 (C-1‴″–6‴″)] were detected in the ^{1}H-^{1}H COSY and HSQC spectral analysis of **13**. Acid hydrolysis of **13** afforded L-arabinose, D-fucose, D-galactose, D-glucose, L-rhamnose, and D-xylose. In the HMBC spectrum of **13**, long-range correlations were observed between H-1‴″ of Glc (δ_H 5.40) and C-2‴″ of Gal (δ_C 81.6) as well as between H-1‴″ of Gal (δ_H 4.98) and C-21 of the aglycone (δ_C 69.9). Thus, **13** was identified as (23*S*,24*S*,25*S*)-24-[(*β*-D-fucopyranosyl)oxy]-21-[*O*-*β*-D-glucopyranosyl-(1→2)-(*β*-D-galactopyranosyl)oxy]-3*β*,23-dihydroxyspirost-5-en-1*β*-yl *O*-*α*-L-rhamnopyranosyl-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

The ^{1}H- and ^{13}C-NMR spectra of **14** ($C_{62}H_{98}O_{34}$) and **15** ($C_{68}H_{108}O_{38}$) indicated their relation to **8** and **10**, respectively, containing a diglycoside composed of Glc and Gal at C-21 of the aglycone, as in **13**. The molecular formula of **14** and **15** were both larger than those of **8** and **10**, respectively, by $C_{12}H_{20}O_{10}$ and acid hydrolysis of **14** yielded L-arabinose, D-galactose, D-glucose, L-rhamnose, and D-xylose. In contrast, acid hydrolysis of **15** afforded L-arabinose, D-fucose, D-galactose, D-glucose, L-rhamnose, and D-xylose. In the HMBC spectra of **14** and **15**, long-range correlations were observed between H-1‴″ of Glc [δ_H 5.38 (**14**); 5.38 (**15**)] and C-2‴″ of Gal [δ_C 81.6 (**14**); 81.8 (**15**)] as well as between H-1‴″ of Gal [δ_H 4.98 (**14**); 4.97 (**15**)] and C-21 of the aglycone [δ_C 69.8 (**14**); 69.8 (**15**)]. Accordingly, **14** and **15** were identified as (23*S*,24*S*,25*S*)-21-[*O*-(*β*-D-glucopyranosyl-(1→2)-*β*-D-galactopyranosyl)-oxy]-3*β*,23,24-trihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside and (23*S*,24*S*,25*S*)-24-[(*β*-D-fucopyranosyl)oxy]-21-[*O*-(*β*-D-glucopyranosyl-(1→2)-*β*-D-galactopyranosyl)oxy]-3*β*,23-dihydroxyspirost-5-en-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, respectively.

The NMR spectral features of **16** ($C_{56}H_{86}O_{27}$), **17** ($C_{50}H_{76}O_{24}$), and **18** ($C_{55}H_{84}O_{28}$) were related to those of **4**, **8**, and **9**, respectively. However, instead of containing three-proton doublet signals for Me-27, as observed in the ^{1}H- and ^{13}C-NMR spectra of **4**, **8**, and **9**, signals arising from an exomethylene group [δ_H 5.23 (brs) and 5.08 (brs) (**16**); 5.05 (brs) and 4.95 (brs) (**17**); 5.20 (brs) and 5.06 (brs) (**18**); δ_C 113.7 (**16**); 112.3 (**17**); 113.9 (**18**)] and quaternary carbon [δ_C 143.8 (**16**); 146.2 (**17**); 143.7 (**18**)] were observed. Therefore, **16**, **17**, and **18** correspond to the C-25/27 dehydroxy derivatives of **4**, **8**, and **9**, respectively, as additionally confirmed by long-range correlations from H_2-27 to C-24, C-25, and C-26 in the associated HMBC spectra. Therefore, **16**, **17**, and **18** were identified as (23*S*,24*S*)-24-[(*β*-D-fucopyranosyl)oxy]-3*β*,23-dihydroxyspirosta-5,25(27)-dien-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, (23*S*,24*S*)-3*β*,21,23,24-tetrahydroxyspirosta-5,25(27)-dien-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, and (23*S*,24*S*)-24-[(*α*-L-arabinopyranosyl)-oxy]-3*β*,21,23-trihydroxyspirosta-5,25(27)-dien-1*β*-yl *O*-*β*-D-apiofuranosyl-(1→3)-*O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, respectively.

Comparison of the ^{1}H- and ^{13}C-NMR spectra **19** ($C_{57}H_{86}O_{29}$) with those of **18** showed considerable structural similarity. Furthermore, the presence of an additional acetyl group to that attached at C-21 of the aglycone was indicated by the ^{1}H- and ^{13}C-NMR spectra [δ_H 1.92 (3H, s); δ_C 170.8 and 20.9]. The ester linkage at aglycone C-21 was formed from acetic acid, as indicated by the long-range correlations between the H_2-21 methylene protons [δ_H 4.37 (m) and 4.34 (m)] and acetyl carbonyl carbon (δ_C 170.8). Thus, **19** was identified as (23*S*,24*S*)-21-acetyloxy-24-[(*α*-L-arabinopyranosyl)oxy]-3*β*,23-dihydroxyspirosta-5,25(27)-dien-1*β*-yl *O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

Analysis of the ^{1}H- and ^{13}C-NMR spectra of **20** ($C_{52}H_{78}O_{25}$) and comparison with those of **19** showed that the aglycone with an acetyloxy group at C-21 and monosaccharide at C-24 were identical to those observed in **19**. However, the ^{1}H- and ^{13}C-NMR signals for the apiofuranosyl group linked to C-3 of the rhamnopyranosyl unit in the sugar moiety attached to the aglycone C-1 were not observed. The ^{1}H- and ^{13}C-NMR spectra of the triglycoside moiety agreed with those observed in the concomitantly isolated spirostanol triglycosides **1**, **2**, **6**, and **7**. Thus, **20** was identified as (23*S*,24*S*)-21-acetyloxy-24-[(*α*-L-arabinopyranosyl)oxy]-3*β*,23-dihydroxyspirosta-5,25(27)-dien-1*β*-yl *O*-(4-*O*-acetyl-*α*-L-rhamnopyranosyl)-(1→2)-*O*-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside.

Compound **21** was obtained as an amorphous powder with a molecular formula was of $C_{38}H_{62}O_{14}$ as determined by HR-ESI-TOF-MS and ^{13}C-NMR data. In the ^{1}H- and ^{13}C-NMR spectra of **21**, signals corresponding to four steroidal methyl groups [δ_H 1.27 (3H, d, J = 7.1 Hz, Me-21), 1.21 (3H, s, Me-19), 0.95 (3H, d, J = 6.5 Hz, Me-27), and 0.90 (3H, s, M-18); δ_C 17.4 (C-27), 16.7 (C-18), 16.3 (C-21), and 14.7 (C-19)], an olefinic group [δ_H 5.55 (1H, brd, J = 4.6 Hz, H-6); δ_C 139.5 (C-5) and 124.7 (C-6)], two anomeric protons and associated carbons [δ_H 4.79 (1H, d, J = 7.7 Hz) and 4.75 (1H, d, J = 7.1 Hz); δ_C 104.8 and 102.2], and a hemiacetal carbon [δ_C 110.6 (C-22)] were observed. These data suggested that **21** was a 22-hydroxyfurostanol glycoside and its enzymatic hydrolysis with naringinase yielded (25*R*)-3*β*-hydroxyspirost-5-en-1*β*-yl *α*-L-arabinopyranoside (**21a**)[22] and D-glucose. In the associated HMBC spectrum, a long-range correlation was observed between H-1″ of the *β*-D-glucopyranosyl unit (δ_H 4.79) and C-26 of the aglycone (δ_C 75.2). Accordingly, **21** was identified as (25*R*)-26-[(*β*-D-glucopyranosyl)oxy]-3*β*,22*α*-dihydroxyfurost-5-en-1*β*-yl *α*-L-arabinopyranoside.

Compounds **12**, **13**, and **15** are spirostanol trisdesmosides, which are types of steroidal glycosides rarely observed in the plant kingdom.

The cytotoxic activities of **1**–**28** were evaluated against HL-60 and A549 cells using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay method. Compound **7** showed cytotoxic activity against HL-60 and A549 cells with IC_{50} values of 5.9 ± 0.46 and 6.6 ± 0.17 μM, respectively. In contrast, **19** was selectively cytotoxic against only A549 cells with an IC_{50} value of 5.5 ± 0.61 μM. Cisplatin was used as a positive control, yielding IC_{50} values of 1.9 and 3.7 μM for HL-60 and A549 cells, respectively. Compounds **1**–**6**, **8**–**18**, and **20**–**28** did not show cytotoxicity against HL-60 and A549 cells at concentrations of up to 10 μM.

Experimental

General Optical rotations were measured on a JASCO P-1030 automatic digital polarimeter (Jasco, Tokyo, Japan). IR spectra were obtained using a JASCO FT-IR 620 spectrophotometer (Jasco). NMR spectra were recorded on a Bruker DRX-500 or AV-600 spectrometer (Bruker, Karlsruhe, Germany) using standard Bruker pulse programs. Chemical shifts (δ) were given with reference to tetramethylsilane (TMS) as an internal standard. HR-ESI-TOF-MS data were obtained using a Water-Micromass LCT mass spectrometer (Waters-Micromass, Manchester, U.K.). CC was conducted by Diaion HP-20 (Mitsubishi-chemical, Tokyo, Japan), silica gel Chromatorex BW-300 (Fuji-Silysia Chemical, Aichi, Japan), and ODS silica gel COSMOSIL 75C_{18}-OPN (Nacalai Tesque, Kyoto, Japan). TLC was carried out precoated silica gel 60 F_{254} or RP_{18} $F_{254}S$ plates (0.25 mm thick) (Merck, Darmstadt, Germany), and the spots were detected by spraying the plates with 10% H_2SO_4 aqueous solution and then heating. HPLC was conducted using a system consisting of a CCPM pump (Shimadzu, Kyoto, Japan), an RI-8021 (Tosoh, Tokyo, Japan) or a Shodex OR-2 (Showa-Denko, Tokyo, Japan) detector, and a Rheodyne injection port (Rohnert Park, CA, U.S.A.). A TSK gel ODS-100Z column (10 mm i.d. $\times$ 250 mm, 5 μm) (Tosoh) was used for the preparative HPLC. Purities of the isolated compounds were verified by MS, TLC, and NMR spectra. The following materials and biochemical grade reagents were used for the cell cultures and cytotoxicity assays: SH-1300 Lab microplate reader (CORONA ELECTRIC, Ibaraki, Japan); 96-well flat-bottom plate (Iwaki Glass, Chiba, Japan); fetal bovine serum (FBS), 0.25% trypsin-ethylenediaminetetraacetic acid (EDTA) solution, RPMI-1640 medium, minimum essential medium (MEM), cisplatin, and MTT (Sigma, St. Louis, MO, U.S.A.); paraformaldehyde and phosphate-buffered saline (PBS) (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan); penicillin G sodium salt and streptomycin sulfate (Gibco, Gland Island, NY, U.S.A.); HL-60 cells (JCRB0085) and A549 cells (JCRB0076) (Human Science Research Resources Bank, Osaka, Japan).

Plant Material The whole plants of *H. foetidus* were purchased from Fuji-engei (Okayama, Japan). A voucher specimen was deposited at the herbarium of the Tokyo University of Pharmacy and Life Sciences (KS-2014-011).[23]

Extraction and Isolation The whole plants of *H. foetidus* (fresh weight, 3.3 kg) were extracted with hot MeOH (10 L). After solvent was removed *in vacuo*, the concentrated MeOH extract (115 g) was fractionated by Diaion HP-20 column and then successively eluted with MeOH/H_2O (3 : 7), MeOH/H_2O (1 : 1), MeOH, EtOH, and EtOAc (each solvent volume 6 L). The MeOH eluate fraction (10 g) was chromatographed on silica gel eluted with stepwise gradient of $CHCl_3$/MeOH/H_2O (90 : 10 : 1, 40 : 10 : 1, 20 : 10 : 1) and finally MeOH alone to get 17 fractions (Frs. 1–17). Fraction 10 was subjected to silica gel CC eluted with $CHCl_3$/MeOH/H_2O (90 : 10 : 1; 40 : 10 : 1) and EtOAc/MeOH/H_2O (80 : 10 : 1; 50 : 10 : 1; 40 : 10 : 1), and ODS silica gel CC eluted with MeOH/H_2O (3 : 2; 1 : 1) and MeCN/H_2O (7 : 3; 1 : 1; 3 : 7; 1 : 3) to yield **1** (35.7 mg), **21** (85.4 mg), **23** (72.1 mg), and **24** (2.9 mg). Fraction 11 was separated by ODS silica gel CC using MeOH/H_2O (4 : 1; 3 : 2) and MeCN/H_2O (1 : 3) to obtain **2** (5.8 mg), **3** (27.0 mg), **6** (3.3 mg), **25** (18.1 mg), and **28** (6.7 mg). Fraction 13 was chromatographed on silica gel eluted with $CHCl_3$/MeOH/H_2O (30 : 10 : 1), ODS silica gel eluted with MeOH/H_2O (3 : 2) and MeCN/H_2O (1 : 3; 1 : 4), and preparative HPLC using MeCN/H_2O (1 : 2; 3 : 7) to furnish **4** (72.1 mg), **5** (2.3 mg), **7** (30.1 mg), **8** (13.0 mg), **20** (8.5 mg), and **26** (85.4 mg). Fraction 14 was fractionated by ODS silica gel CC using MeOH/H_2O (3 : 2; 11 : 9; 1 : 1) and MeCN/H_2O (1 : 3; 1 : 4), and preparative HPLC using MeCN/H_2O (3 : 7; 1 : 3) to acquire **16** (16.2 mg), **17** (6.1 mg), **19** (28.6 mg), **22** (16.6 mg), and **27** (4.9 mg). Fraction 15 was separated by ODS silica gel CC eluted with MeOH/H_2O (11 : 9; 1 : 1) and MeCN/H_2O (1 : 3; 1 : 4), and preparative HPLC using MeCN/H_2O (1 : 3) to afford **9** (26.9 mg) and **10** (6.8 mg). Fraction 16 was chromatographed on ODS silica gel using MeOH/H_2O (11 : 9; 9 : 11) and MeCN/H_2O (1 : 3; 1 : 4) to collect **11** (3.9 mg) and **18** (46.3 mg). Fraction 17 was subjected to silica gel CC eluted with $CHCl_3$/MeOH/H_2O (20 : 10 : 1; 10 : 10 : 1), ODS silica gel CC eluted with MeOH/H_2O (1 : 1) and MeCN/H_2O (1 : 3; 1 : 4), and preparative HPLC using MeCN/H_2O (1 : 3; 1 : 4) to furnish **12** (12.9 mg), **13** (7.0 mg), **14** (19.9 mg), and **15** (15.9 mg).

Compound 1 Amorphous powder; $[\alpha]_D^{25}$ −94.4 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3392 (OH), 2926 (CH), 1729 (C=O); ^{1}H- (500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 937.4412 $[M + Na]^+$ (Calcd for $C_{45}H_{70}NaO_{19}$: 937.4409).

Compound 2 Amorphous powder; $[\alpha]_D^{25}$ −14.5 ($c = 0.05$, MeOH); IR ν_{max} (film) cm^{-1}: 3370 (OH), 2925 (CH), 1730 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1083.4980 $[M + Na]^+$ (Calcd for $C_{51}H_{80}NaO_{23}$: 1083.4988).

Compound 3 Amorphous powder; $[\alpha]_D^{25}$ −23.4 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3375 (OH), 2930 (CH), 1727 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1069.4832 $[M + Na]^+$ (Calcd for $C_{50}H_{78}NaO_{23}$: 1069.4832).

Compound 4 Amorphous powder; $[\alpha]_D^{25}$ −31.7 ($c = 0.11$, MeOH); IR ν_{max} (film) cm^{-1}: 3375 (OH), 2927 (CH), 1727 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1215.5405 $[M + Na]^+$ (Calcd for $C_{56}H_{88}NaO_{27}$: 1215.5411).

Compound 5 Amorphous powder; $[\alpha]_D^{25}$ −8.7 ($c = 0.14$, MeOH); IR ν_{max} (film) cm^{-1}: 3374 (OH), 2925 (CH); ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1057.4819 $[M + Na]^+$ (Calcd for $C_{49}H_{78}NaO_{23}$: 1057.4832).

Compound 6 Amorphous powder; $[\alpha]_D^{25}$ −30.5 ($c = 0.05$, MeOH); IR ν_{max} (film) cm^{-1}: 3364 (OH), 2925 (CH), 1725 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-

(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 953.4354 $[M+Na]^+$ (Calcd for $C_{45}H_{70}NaO_{20}$: 953.4358).

Compound 7 Amorphous powder; $[\alpha]_D^{25}$ −42.0 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3383 (OH), 2922 (CH), 1728 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1099.4934 $[M+Na]^+$ (Calcd for $C_{51}H_{80}NaO_{24}$: 1099.4937).

Compound 8 Amorphous powder; $[\alpha]_D^{25}$ −13.9 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3389 (OH), 2924 (CH), 1729 (C=O); ^{1}H- (500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1085.4775 $[M+Na]^+$ (Calcd for $C_{50}H_{78}NaO_{24}$: 1085.4781).

Compound 9 Amorphous powder; $[\alpha]_D^{25}$ −62.5 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3388 (OH), 2925 (CH), 1731 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1217.5203 $[M+Na]^+$ (Calcd for $C_{55}H_{86}NaO_{28}$: 1217.5203).

Compound 10 Amorphous powder; $[\alpha]_D^{25}$ −41.9 ($c = 0.05$, MeOH); IR ν_{max} (film) cm^{-1}: 3389 (OH), 2925 (CH), 1731 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1231.5364 $[M+Na]^+$ (Calcd for $C_{56}H_{88}NaO_{28}$: 1231.5360).

Compound 11 Amorphous powder; $[\alpha]_D^{25}$ −8.8 ($c = 0.05$, MeOH); IR ν_{max} (film) cm^{-1}: 3357 (OH), 2926 (CH), 1731 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1247.5299 $[M+Na]^+$ (Calcd for $C_{56}H_{88}NaO_{29}$: 1247.5309).

Compound 12 Amorphous powder; $[\alpha]_D^{25}$ −22.7 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3357 (OH), 2930 (CH), 1732 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1379.5753 $[M+Na]^+$ (Calcd for $C_{61}H_{96}NaO_{33}$: 1379.5732).

Compound 13 Amorphous powder; $[\alpha]_D^{25}$ −17.7 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3364 (OH), 2927 (CH); ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1381.5883 $[M+Na]^+$ (Calcd for $C_{61}H_{98}NaO_{33}$: 1381.5888).

Compound 14 Amorphous powder; $[\alpha]_D^{25}$ −34.1 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3360 (OH), 2925 (CH), 1730 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1409.5863 $[M+Na]^+$ (Calcd for $C_{62}H_{98}NaO_{34}$: 1409.5837).

Compound 15 Amorphous powder; $[\alpha]_D^{25}$ −32.0 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3373 (OH), 2931 (CH), 1731 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1555.6422 $[M+Na]^+$ (Calcd for $C_{68}H_{108}NaO_{38}$: 1555.6416).

Compound 16 Amorphous powder; $[\alpha]_D^{25}$ −69.1 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3389 (OH), 2932 (CH), 1732 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1213.5251 $[M+Na]^+$ (Calcd for $C_{56}H_{86}NaO_{27}$: 1213.5254).

Compound 17 Amorphous powder; $[\alpha]_D^{25}$ −94.4 ($c = 0.05$, MeOH); IR ν_{max} (film) cm^{-1}: 3375 (OH), 2925 (CH), 1731 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1083.4623 $[M+Na]^+$ (Calcd for $C_{50}H_{76}NaO_{24}$: 1083.4624).

Compound 18 Amorphous powder; $[\alpha]_D^{25}$ −125.4 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3404 (OH), 2923 (CH), 1728 (C=O); ^{1}H- (500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1215.5081 $[M+Na]^+$ (Calcd for $C_{55}H_{84}NaO_{28}$: 1215.5047).

Compound 19 Amorphous powder; $[\alpha]_D^{25}$ −110.3 ($c = 0.10$, MeOH); IR ν_{max} (film) cm^{-1}: 3393 (OH), 2924 (CH), 1733 (C=O); ^{1}H- (500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(500 MHz, C_5D_5N) and ^{13}C-NMR (125 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1257.5111 $[M+Na]^+$ (Calcd for $C_{57}H_{86}NaO_{29}$: 1257.5152).

Compound 20 Amorphous powder; $[\alpha]_D^{25}$ −43.6 ($c = 0.025$, MeOH); IR ν_{max} (film) cm^{-1}: 3406 (OH), 2923 (CH), 1720 (C=O); ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar and acetyl moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 1125.4730 $[M+Na]^+$ (Calcd for $C_{52}H_{78}NaO_{25}$: 1125.4730).

Compound 21 Amorphous powder; $[\alpha]_D^{25}$ −10.7 ($c = 0.11$, MeOH); IR ν_{max} (film) cm^{-1}: 3364 (OH), 2925 (CH); ^{1}H-(600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the aglycone moiety, see Tables 1, 2; ^{1}H- (600 MHz, C_5D_5N) and ^{13}C-NMR (150 MHz, C_5D_5N) data of the sugar moieties, see Tables 3, 4; HR-ESI-TOF-MS *m/z*: 765.4035 $[M+Na]^+$ (Calcd for $C_{38}H_{62}NaO_{14}$: 765.4037).

Acid Hydrolysis of 1–20 Compound **1** (10.0 mg), **2** (2.0 mg), **3** (3.6 mg), **4** (4.0 mg), **5** (1.9 mg), **6** (1.1 mg), **7** (10.0 mg), **8** (5.0 mg), **9** (5.5 mg), **10** (2.3 mg), **11** (2.5 mg), **12** (4.7 mg), **13** (4.0 mg), **14** (5.0 mg), **15** (5.0 mg), **16** (4.8 mg), **17** (2.4 mg), **18** (10.0 mg), **19** (5.0 mg), and **20** (2.8 mg) were independently dissolved in 0.2 M HCl or 0.5 M HCl (dioxane/H_2O, 1 : 1) and heated at 95°C for 30 min under an Ar atmosphere. Each reaction mixture was neutralized by passing through an Amberlite IRA-96 (Organo, Tokyo, Japan) column, was subjected to Diaion HP-20 CC eluted with MeOH/H_2O (2 : 3) and finally Me_2CO/EtOH (1 : 1) to obtain sugar fractions (3.3 mg from **1**; 0.79 mg from **2**; 1.4 mg from **3**; 2.9 mg from **4**; 0.77 mg from **5**; 0.38 mg from **6**; 4.5 mg from **7**; 2.8 mg from **8**; 2.3 mg from **9**; 0.92 mg from **10**; 0.8 mg from **11**; 2.3 mg from **12**; 2.0 mg from **13**; 2.5 mg from **14**; 2.6 mg from **15**; 2.1 mg from **16**; 0.94 mg from **17**; 3.8 mg from **18**; 1.9 mg from **19**; and 1.0 mg from **20**). The sugar fractions were analyzed by HPLC under the following conditions: column, Capcell Pak NH_2 UG80 (4.6 mm i.d. $\times$250 mm, 5 μm, Shiseido, Tokyo, Japan); solvent, MeCN/H_2O (17 : 3); detection, refractive index and optical rotation; flow rate, 1.0 mL/min. D-Apiose in **3**, **4**, **8**–**12**, and **14**–**19**, L-arabinose in **1**–**20**, D-fucose in **4**, **7**, **10**, **13**, **15**, and **16**, D-galactose in **11**–**15**, D-glucose in **5** and **13**–**15**, D-quinovose in **2**, L-rhamnose in **1**–**20**, and D-xylose in **1**–**20** were identified by comparing their retention times (t_R) and optical rotations with those of authentic samples: D-apiose (6.66, positive optical rotation), L-rhamnose (7.64, negative optical rotation), D-fucose (8.42, positive optical rotation), D-quinovose (8.78, positive optical rotation), L-arabinose (9.57, positive optical rotation), D-xylose (9.92, positive optical rotation), D-galactose (15.63, positive optical rotation), and D-glucose (16.14, positive optical rotation).

Enzymatic Hydrolysis of 21 Compound **21** (15.0 mg) was treated with naringinase (45.0 mg, EC 232-962-4, Sigma) in AcOH/AcOK buffer (pH 4.3, 5.0 mL) at 28°C for 84 h. The reaction mixture was purified by silica gel CC using $CHCl_3$/MeOH/H_2O (90 : 10 : 1) to yield **21a** (12.2 mg) and a sugar fraction (1.3 mg). HPLC analysis of the sugar fraction under the same conditions as those of **1** showed the presence of D-glucose (16.14, positive optical rotation).

Cytotoxic Activity Assay HL-60 and A549 cells were kept in RPMI-1640 medium and MEM, respectively. These cell media contained 100 μg/mL streptomycin sulfate, penicillin G sodium salt, and heat-inactivated 10% FBS supplemented with L-glutamine. Cytotoxic activity of the isolated compounds against HL-60 and A549 cells was evaluated by a modified MTT assay method as previously reported.[24)]

Conflict of Interest The authors declare no conflict of interest.

Supplementary Materials The online version of this article contains supplementary materials.

References

1) "The Grand Dictionary of Horticulture," Vol. 4, ed. by Tsukamoto Y., Shogakukan, Tokyo, 1989, pp. 387–389.
2) Bassarello C., Muzashvili T., Skhirtladze A., Kemertelidze E., Pizza C., Piacente S., *Phytochemistry*, **69**, 1227–1233 (2008).
3) Muzashvili T., Perrone A., Napolitano A., Kemertelidze E., Pizza C., Piacente S., *Phytochemistry*, **72**, 2180–2188 (2011).
4) Kißmer B., Wichtl M., *Planta Med.*, **52**, 152–153 (1986).
5) Tsiftsoglou S. O., Stefanakis K. M., Lazari M. D., *Biochem. Syst. Ecol.*, **79**, 8–11 (2018).
6) Yang F. Y., Su Y. F., Wang Y., Chai X., Han X., Wu Z. H., Gao X. M., *Biochem. Syst. Ecol.*, **38**, 759–763 (2010).
7) Yang J., Zhang Y. H., Miao F., Zhou L., Sun W., *Fitoterapia*, **81**, 636–639 (2010).
8) Zhang H., Su Y., Yang F., Zhao Z., Gao X., *Phytochem. Lett.*, **10**, 164–167 (2014).
9) Meng Y., Whiting P., Šik V., Rees H. H., Dinan L., *Phytochemistry*, **57**, 401–407 (2001).
10) Watanabe K., Mimaki Y., Sakagami H., Sashida Y., *J. Nat. Prod.*, **66**, 236–241 (2003).
11) Yokosuka A., Iguchi T., Kawahata R., Mimaki Y., *Phytochem. Lett.*, **23**, 94–99 (2018).
12) Mimaki Y., Watanabe K., Sakuma S., Sakagami H., Sashida Y., *Helv. Chim. Acta*, **86**, 398–407 (2003).
13) Watanabe K., Sakagami H., Mimaki Y., *Heterocycles*, **65**, 775–785 (2005).
14) Mimaki Y., Matsuo Y., Watanabe K., Sakagami H., *J. Nat. Med.*, **64**, 452–459 (2010).
15) Zhang H., Su Y. F., Yang F. Y., Zhao Z. Q., Gao X. M., *Helv. Chim. Acta*, **97**, 1652–1665 (2014).
16) Zhang H., Su Y. F., Yang F. Y., *Nat. Prod. Res.*, **30**, 1724–1730 (2016).
17) Zhang H., Su Y. F., Yang F. Y., *Phytochem. Lett.*, **18**, 213–219 (2016).
18) Zhang H., Su Y. F., Yang F. Y., Gao X. M., *Nat. Prod. Res.*, **31**, 925–931 (2017).
19) Asano T., Murayama T., Hirai Y., Shoji J., *Chem. Pharm. Bull.*, **41**, 566–570 (1993).
20) Mimaki Y., Inoue T., Kuroda M., Sashida Y., *Phytochemistry*, **43**, 1325–1331 (1996).
21) Yang Q. X., Zhang Y. J., Li H. Z., Yang C. R., *Steroids*, **70**, 732–737 (2005).
22) Watanabe Y., Sanada S., Ida Y., Shoji J., *Chem. Pharm. Bull.*, **31**, 3486–3495 (1983).
23) Iguchi T., Kuroda M., Naito R., Watanabe T., Matsuo Y., Yokosuka A., Mimaki Y., *Molecules*, **22**, e1243 (2017).
24) Iguchi T., Kuroda M., Naito R., Watanabe T., Matsuo Y., Yokosuka A., Mimaki Y., *J. Nat. Med.*, **73**, 131–145 (2019).