Three New Glycosides from *Viburnum plicatum* THUNB. var. *tomentosum* MIQ.

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Three new glycosides, 7-*O*-tigloylsecologanol (**1**), 7-*O*-tigloylsecologanolic acid (**2**), and 3′-*O*-[(2*S*)-2-methylbutanoyl]henryoside (**3**), together with seven known ones, were isolated from the leaves of *Viburnum plicatum* THUNB. var. *tomentosum* MIQ. Their structures were established on the basis of spectral and chemical data.

Introduction. – The deciduous shrub *Viburnum plicatum* THUNB. var. *tomentosum* MIQ. (Caprifoliaceae) is widely distributed in Japan and China. This plant has been utilized in traditional Chinese medicine (Chinese name, hú dié shù) for lymphadenitis, ringworm, and infantile tantrum [1]. In a continuation of our investigation of the chemical constituents from plants of the genus *Viburnum* species [2–9], we have now examined the chemical constituents of the leaves of *V. plicatum* THUNB. var. *tomentosum* MIQ. As far as we know, there is no report regarding the chemical constituents of this plant. In this article, we describe the isolation and structure elucidation of three new glycosides, named 7-*O*-tigloylsecologanol[1]) (**1**), 7-*O*-tigloylsecologanolic acid[1]) (**2**), and 3′-*O*-[(2*S*)-2-methylbutanoyl]henryoside[1]) (**3**), together with seven known ones, which were isolated from the leaves of this plant. This article deals with the structural elucidation and identification of these compounds.

Results and Discussion. – The MeOH extract of the leaves of *V. plicatum* THUNB. var. *tomentosum* MIQ. was partitioned with $CHCl_3$, AcOEt, BuOH, and H_2O. The BuOH- and AcOEt-soluble fractions were each subjected to separation by a combination of chromatographic procedures. From the BuOH-soluble fraction, compounds **1**–**3** and **4**[2]) were isolated, while compounds **5**–**10**[2]) were isolated from the AcOEt-soluble fraction. The known compounds **4**–**10**[2]) were identified as (4*R*)-α-terpineol *O*-β-D-glucopyranoside[2]) (**4**) [10], (7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-D-glucopyranoside[2]) (**5**) [11], (7*R*,8*S*)-dihydrodehydrodiconiferyl alcohol 9-*O*-β-D-glucopyranoside[2]) (**6**) [12], quercetin 3-*O*-robinobioside[2]) (**7**) [13], quercetin 3-*O*-rutinoside[2]) (**8**) [13], kaempferol 3-*O*-robinobioside[2]) (**9**) [13], and kaempferol 3-*O*-rutinoside[2]) (**10**) [13], respectively, by comparison of their spectroscopic data with those previously described in the literatures.

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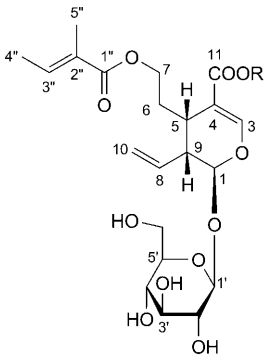
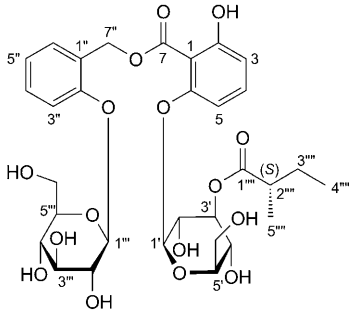
[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

[2]) For formulas, see corresponding references.



1[1]) R = Me
2[1]) R = H



3[1])

Compound **1** was obtained as an optically active amorphous powder. The molecular formula of **1**, $C_{22}H_{32}O_{11}$, was confirmed by HR-FAB-MS (*m/z* 495.1855 ($[M+Na]^+$)). The ^{1}H-NMR spectrum of **1** (*Table 1*) showed signals due to one olefinic H-atom at

Table 1. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; in CD_3OD) *of* **1** *and* **2**[1]). δ in ppm, *J* in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	5.56 (*d*, *J* = 6.6)	97.7	5.53 (*d*, *J* = 6.3)	97.6
H–C(3)	7.47 (*s*)	153.7	7.46 (*s*)	153.2
C(4)	–	111.5	–	112.1
H–C(5)	2.91 (br. *dd*, *J* = 6.6, 6.0)	31.5	2.89 (br. *dd*, *J* = 6.6, 5.9)	31.3
CH_2(6)	1.86 (br. *ddd*, *J* = 13.7, 6.6, 6.0), 2.03 (br. *ddd*, *J* = 13.7, 7.3, 6.0)	30.2	1.84 (overlapped), 2.08 (br. *ddd*, *J* = 13.9, 7.1, 5.9)	30.1
CH_2(7)	4.14 (br. *dt*, *J* = 11.2, 6.6), 4.16 (*ddd*, *J* = 11.2, 7.3, 6.0)	64.2	4.14 (br. *dt*, *J* = 11.0, 6.6), 4.19 (*ddd*, *J* = 11.0, 7.1, 5.9)	64.3
H–C(8)	5.79 (*ddd*, *J* = 17.3, 10.5, 8.5)	135.8	5.79 (*ddd*, *J* = 17.3, 10.5, 8.5)	135.9
H–C(9)	2.65 (*ddd*, *J* = 8.5, 6.6, 6.0)	45.6	2.65 (*ddd*, *J* = 8.5, 6.3, 5.9)	45.5
CH_2(10)	5.25 (*dd*, *J* = 10.5, 1.0), 5.30 (*dd*, *J* = 17.3, 1.0)	119.6	5.25 (*dd*, *J* = 10.5, 1.2), 5.29 (*dd*, *J* = 17.3, 1.2)	119.5
C(11)	–	169.2	–	171.2
MeO–C(11)	3.67 (*s*)	51.8	–	–
H–C(1′)	4.69 (*d*, *J* = 7.8)	100.2	4.69 (*d*, *J* = 7.8)	100.2
H–C(2′)	3.18 (*dd*, *J* = 9.0, 7.8)	74.7	3.19 (*dd*, *J* = 9.0, 7.8)	74.7
H–C(3′)	3.30 (overlapped)	78.5	3.30 (overlapped)	78.5
H–C(4′)	3.30 (overlapped)	71.6	3.30 (overlapped)	71.6
H–C(5′)	3.30 (overlapped)	78.1	3.30 (overlapped)	78.0
CH_2(6′)	3.66 (overlapped), 3.90 (*dd*, *J* = 12.0, 2.0)	62.8	3.66 (*dd*, *J* = 12.0, 5.9), 3.90 (*dd*, *J* = 12.0, 2.0)	62.8
C(1″)	–	169.6	–	169.7
C(2″)	–	129.7	–	129.7
H–C(3″)	6.85 (br. *dq*, *J* = 7.3, 1.2)	138.7	6.86 (br. *dq*, *J* = 7.0, 1.2)	138.6
Me(4″)	1.80 (br. *d*, *J* = 7.3)	14.4	1.79 (br. *dd*, *J* = 7.0, 1.2)	14.4
Me(5″)	1.81 (br. *s*)	12.1	1.81 (br. *q*, *J* = 1.2)	12.1

δ(H) 7.47 (*s*, H−C(3[1])), vinyl H-atoms at δ(H) 5.25 (*dd*, J = 10.5, 1.0 Hz, H_a−C(10)), 5.30 (*dd*, J = 17.3, 1.0 Hz, H_b−C(10)), and 5.79 (*ddd*, J = 17.3, 10.5, 8.5 Hz, H−C(8)), two acetal H-atoms at δ(H) 4.69 (*d*, J = 7.8 Hz, H−C(1′)) and 5.56 (*d*, J = 6.6 Hz, H−C(1)), one MeO group at δ(H) 3.67 (*s*, MeO−C(11)), two CH_2 groups at δ(H) 1.86 (br. *ddd*, J = 13.7, 6.6, 6.0 Hz, H_a−C(6)), 2.03 (br. *ddd*, J = 13.7, 7.3, 6.0 Hz, H_b−C(6)), 4.14 (br. *dt*, J = 11.2, 6.6 Hz, H_a−C(7)), and 4.16 (*ddd*, J = 11.2, 7.3, 6.0 Hz, H_b−C(7)), and two CH groups at δ(H) 2.91 (br. *dd*, J = 6.6, 6.0 Hz, H−C(5)) and 2.65 (*ddd*, J = 8.5, 6.6, 6.0 Hz, H−C(9)). The ^{1}H,^{1}H-COSY experiment of **1** in combination with the HMQC spectrum revealed the partial structures shown by the bold lines in *Fig. 1*. Acid hydrolysis of **1** yielded D-glucose which was identified by its retention time and optical rotation by means of chiral detection in HPLC analysis. The ^{1}H- and ^{13}C-NMR data (*Table 1*) were closely related to those of secologanol = (2*S*,3*R*,4*S*)-3-ethenyl-2-(*β*-D-glucopyranosyloxy)-3,4-dihydro-4-(2-hydroxyethyl)-2*H*-pyran-5-carboxylic acid methyl ester [14], except for the presence of signals due to a tigloyl group (δ(H) 6.85 (*dq*, J = 7.3, 1.2 Hz, H−C(3″)), 1.81 (br. *s*, Me(5″)), and 1.80 (br. *d*, J = 7.3 Hz, Me(4″)); δ(C) 169.6 (C(1″)), 138.7 (C(3″)), 129.7 (C(2″)), 14.4 (C(4″)), and 12.1 (C(5″)). Furthermore, the ^{1}H- and ^{13}C-NMR chemical shifts of the CH_2(7) moiety of **1** were shifted downfield by +0.6 ppm (2 H−C(7)) and +2.9 ppm (C(7)) compared with those of secologanol, suggesting that the additional tigloyl group in **1** is located at OH−C(7) of secologanol. This finding was supported by the HMBC cross-peaks between CH_2(7) and C(1″). Other HMBC and ^{1}H,^{1}H-COSY (*Fig. 1*), and NOESY (H−C(1)/H−C(8), H−C(5)/H−C(9)) correlations of **1** confirmed the proposed structure. The absolute configuration of the aglycone of **1** was not determined. From the above data, the structure of **1** was established as *rel*-(2*R*,3*S*,4*R*)-3-ethenyl-2-(*β*-D-glucopyranosyloxy)-3,4-dihydro-4-{2-[(2-methylbut-2-enoyl)oxy]ethyl}-2*H*-pyran-5-carboxylic acid methyl ester, and named 7-*O*-tigloylsecologanol.

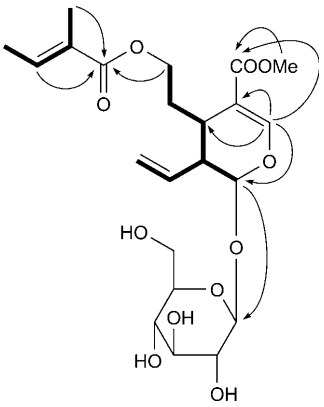


Fig. 1. *^{1}H,^{1}H-COSY Correlations* (bold line) *and key HMBCs* (full-line arrows) *of* **1**

Compound **2** was obtained as an optically active amorphous powder. In the HR-FAB-MS, the *m*/*z* at 481.1671 ([*M* + Na]$^+$) indicated the molecular formula of **2** as $C_{21}H_{30}O_{11}$. Acid hydrolysis of **2** in the above described manner gave only D-glucose. The ^{1}H- and ^{13}C-NMR spectra of **2** (*Table 1*) closely resembled those of **1**, except for

the absence of signals for a MeO group. A comparison of the ^{13}C-NMR chemical shifts of **1** and **2** indicated that the C(11)=O group (δ(C) 171.2) of **2** was deshielded by 2.0 ppm with respect to that of **1**. The molecular formula of **2** represented a loss of a CH_2 unit compared to that of **1**. These findings suggested that **2** is the de-*O*-methyl analogue of **1**. The complete assignments of the ^{1}H- and ^{13}C-NMR signals of **2** were confirmed by the ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments (*Fig. 2*). The absolute configuration of the aglycone of **2** was not determined. From the above data, the structure of **2** was established as *rel*-(2*R*,3*S*,4*R*)-3-ethenyl-2-(β-D-glucopyranosyloxy)-3,4-dihydro-4-{2-[(2-methylbut-2-enoyl)oxy]ethyl}-2*H*-pyran-5-carboxylic acid, and named 7-*O*-tigloylsecologanolic acid.

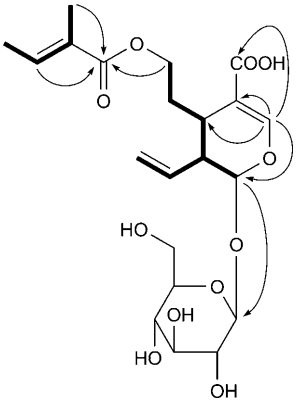


Fig. 2. *^{1}H,^{1}H-COSY Correlations* (bold line) *and key HMBCs* (full-line arrows) *of* **2**

Compound **3** was obtained as an optically active amorphous powder. The molecular formula of **3**, $C_{31}H_{40}O_{16}$, was confirmed by HR-FAB-MS (*m/z* 691.2207 ($[M+Na]^+$)). The ^{1}H-NMR spectrum of **3** (*Table 2*) showed the signals due to one 1,2,6-trisubstituted aromatic ring at δ(H) 6.60 (*dd*, $J=8.5$, 1.0 Hz, H–C(5)), 6.74 (*dd*, $J=8.3$, 1.0 Hz, H–C(3)), and 7.28 (*dd*, $J=8.5$, 8.3 Hz, H–C(4)), one *ortho*-disubstituted aromatic ring at δ(H) 7.06 (*dt*, $J=7.6$, 1.0 Hz, H–C(5″)), 7.21 (*dd*, $J=8.3$, 1.0 Hz, H–C(3″)), 7.32 (*ddd*, $J=8.3$, 7.6, 1.5 Hz, H–C(4″)), and 7.54 (*dd*, $J=7.6$, 1.5 Hz, H–C(6″)), one CH_2 as an *AB* system at δ(H) 5.48 (*d*, $J=13.0$ Hz, H_a–C(7″)) and 5.53 (*d*, $J=13.0$ Hz, H_b–C(7″)), and two anomeric H-atoms at δ(H) 4.94 (*d*, $J=7.8$ Hz, H–C(1‴)) and 5.03 (*d*, $J=7.8$ Hz, H–C(1′)). Acid hydrolysis of **3** in the above described manner gave only D-glucose. The coupling constants of the two anomeric H-atoms indicated that the glycosyl linkages are of β-configuration. These spectral features were almost identical to those of henryoside = 2-{{[2-(β-D-glucopyranosyloxy)-6-hydroxybenzoyl]oxy}methyl}phenyl β-D-glucopyranoside isolated from *V. henryi* [15]. This was also supported by the HMBC correlations shown in *Fig. 3*.

The ^{1}H- and ^{13}C-NMR spectra of **3** (*Table 2*), however, showed the presence of additional signals due to one C=O group (δ(C) 178.1 (C(1⁗))), one primary Me group (δ(H) 0.98 (*t*, $J=7.1$ Hz, Me(4⁗); δ(C) 12.0 (C(4⁗))), one secondary Me group (δ(H) 1.19 (*d*, $J=7.1$ Hz, Me(5⁗); δ(C) 17.0 (C(5⁗))), one CH_2 group (δ(H) 1.54 (*dquint.*, $J=14.6$, 7.1 Hz, H_a–C(3⁗)) and 1.74 (*dquint.*, $J=14.6$, 7.1 Hz, H_b–C(3⁗)); δ(C) 28.1

Table 2. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; in CD_3OD) *of* **3**[1]). δ in ppm, J in Hz.

	δ(H)	δ(C)		δ(H)	δ(C)
C(1)	–	110.7	H–C(3″)	7.21 (*dd*, *J* = 8.3, 1.0)	116.6
C(2)	–	158.1	H–C(4″)	7.32 (*ddd*, *J* = 8.3, 7.6, 1.5)	130.8
H–C(3)	6.74 (*dd*, *J* = 8.3, 1.0)	107.7	H–C(5″)	7.06 (*dt*, *J* = 7.6, 1.0)	123.6
H–C(4)	7.28 (*dd*, *J* = 8.5, 8.3)	134.2	H–C(6″)	7.54 (*dd*, *J* = 7.6, 1.5)	130.7
H–C(5)	6.60 (*dd*, *J* = 8.5, 1.0)	111.8	CH_2(7″)	5.48, 5.53 (*d*, *J* = 13.0, each)	63.7
C(6)	–	160.1	H–C(1‴)	4.94 (*d*, *J* = 7.8)	102.9
C(7)	–	170.0	H–C(2‴)	3.16–3.54 (overlapped)	74.9
H–C(1′)	5.03 (*d*, *J* = 7.8)	102.4	H–C(3‴)	3.16–3.54 (overlapped)	78.3
H–C(2′)	3.16–3.54 (overlapped)	73.1	H–C(4‴)	3.16–3.54 (overlapped)	71.3
H–C(3′)	4.99 (*t*, *J* = 9.3)	78.2	H–C(5‴)	3.16–3.54 (overlapped)	78.0
H–C(4′)	3.16–3.54 (overlapped)	69.4	CH_2(6‴)	3.70 (*dd*, *J* = 12.2, 4.8), 3.88 (*dd*, *J* = 12.2, 1.7)	62.2
H–C(5′)	3.16–3.54 (overlapped)	78.1	C(1⁗)	–	178.1
CH_2(6′)	3.67 (*dd*, *J* = 12.0, 4.6), 3.83 (*dd*, *J* = 12.0, 1.2)	62.5	H–C(2⁗)	2.48 (*sext.*, *J* = 7.1)	42.6
C(1″)	–	126.7	CH_2(3⁗)	1.54 (*dquint.*, *J* = 14.6, 7.1), 1.74 (*dquint.*, *J* = 14.6, 7.1)	28.1
C(2″)	–	156.9	Me(4⁗)	0.98 (*t*, *J* = 7.1)	12.0
			Me(5⁗)	1.19 (*d*, *J* = 7.1)	17.0

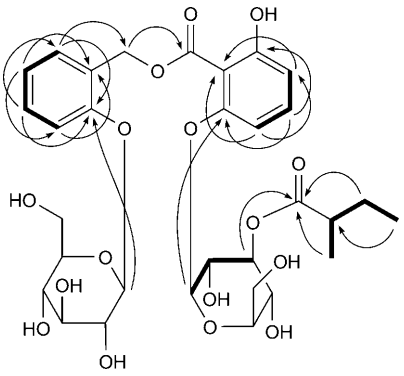
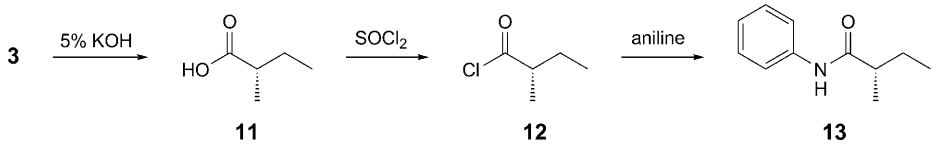


Fig. 3. *^{1}H,^{1}H-COSY correlations* (bold line) *and key HMBCs* (full-line arrows) *of* **3**

(C(3⁗))), and one CH group (δ(H) 2.48 (*sext.*, *J* = 7.1 Hz, H–C(2⁗)); δ(C) 42.6 (C(2⁗))). Detailed analysis of the ^{1}H- and ^{13}C-NMR spectra of the additional signals were undertaken with the aid of ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments (*Fig. 3*), suggesting the additional moiety to be a 2-methylbutanoyl moiety. From the findings presented above, compound **3** was deduced to be a 2-methylbutanoic acid ester of henryoside. The additional 2-methylbutanoyl moiety of **3** is attached to OH–C(3′) of henryoside as established by the HMBC between H–C(3′) (δ(H) 4.99) and C(1⁗). Other HMBCs (*Fig. 3*) confirmed the planar structure of **3**. To determined the absolute configuration at C(2⁗) of the 2-methylbutanoyl moiety of **3**, we referred to a reported HPLC method by means of a chiral column [16]. Briefly, alkaline hydrolysis of **3** was carried out to afford 2-methylbutanoic acid (**11**), which was converted into the

corresponding acyl chloride **12** with $SOCl_2$. Treatment of **12** with aniline (= benzenamine) afforded amide **13** (*Scheme*). The (2*S*)-2-methyl-*N*-phenylbutanamide and racemic (2*RS*)-2-methyl-*N*-phenylbutanamide were synthesized from commercial (2*S*)-2-methylbutanoic acid and (2*RS*)-2-methylbutanoic acid as described for **13** above. The (2*RS*)-methyl-*N*-phenylbutanamide was separated into its enantiomers by HPLC with a chiral column. Comparison of the retention time of **13** with the synthetic (2*S*)-2-methyl-*N*-phenylbutanamide and racemic (2*RS*)-2-methyl-*N*-phenylbutanamide revealed the absolute configuration at C(2‴) of the 2-methylbutanoyl moiety of **3** to be (*S*). From the above data, the structure of **3** was established as 2″-(*β*-D-glucopyranosyloxy)benzyl 2-hydroxy-6-{{3-*O*-[(2*S*)-2-methylbutanoyl]-*β*-D-glucopyranosyl}oxy}benzoate, and named 3′-*O*-[(2*S*)-2-methylbutanoyl]henryoside.

Scheme. *Synthesis of (2*S*)-2-Methyl-*N*-phenylbutanamide* (**13**) *from* **3**



11 **12** **13**

We thank Mrs. *S. Sato* and *T. Matsuki* of Tohoku Pharmaceutical University for NMR and MS measurements.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 70–230 mesh; *Merck*) and *Sephadex LH-20* (*Pharmacia Fine Chemicals*). HPLC: *Tosoh-8020* apparatus; *TSKgel-ODS-80TM* column (5 μm, 6.0 mm i.d. × 15 cm; *Tosoh*), *TSKgel-ODS-120T* column (10 μm, 7.8 mm i.d. × 30 cm; *Tosoh*), and *Cosmosil-5SL* column (5 μm, 10 mm i.d. × 25 cm; *Nacalai tesque*); t_R in min. Optical rotation: *Jasco-DIP-360* digital polarimeter. UV Spectra: *Beckman-DU-64* spectrometer; λ_{max} (log ε) in nm. NMR Spectra: *Jeol-JNM-GSX-400* spectrometer; δ in ppm rel. to Me_4Si; *J* in Hz. EI-, HR-EI-, FAB-, and HR-FAB-MS: *Jeol-JMS-303* mass spectrometer; in *m*/*z* (rel. %), with glycerol as matrix for FAB.

Plant Material. Leaves of *Viburnum plicatum* THUNB. var. *tomentosum* MIQ. were collected in June 2007 in Sendai, Miyagi prefecture, Japan, and identified by *M. K.* A voucher specimen is deposited in the laboratory of *M. K.* (No. 2007-6-KM2).

Extraction and Isolation. Fresh leaves of *V. plicatum* THUNB. var. *tomentosum* MIQ. (450 g) were extracted two times consecutively (10 d each time) with MeOH (2 × 8 l) at r.t. The MeOH extract was concentrated and the residue (41.7 g) suspended in H_2O (500 ml). This suspension was successively extracted with $CHCl_3$ (3 × 500 ml), AcOEt (3 × 500 ml), and BuOH (3 × 500 ml). The AcOEt-soluble fraction (3.1 g) was subjected to CC (*Sephadex LH-20*, 50% MeOH), and the eluate was separated into *Fractions 1–13*. *Fr. 3* was subjected to prep. HPLC (*TSKgel-ODS-80TM*, MeOH/H_2O 1:2, flow rate 1.0 ml/min, column temp. 40°, detection at 205 nm) to give five *Peaks 1–5*. *Peak 3* (t_R 48) was purified by prep. HPLC (*Cosmosil-5SL*, CH_2Cl_2/MeOH/H_2O 80:10:1, flow rate 1.5 ml/min, r.t., detection at 225 nm): **2** (10.5 mg; t_R 35.4). *Peak 4* (t_R 65) was purified by prep. HPLC (*Cosmosil-5SL*, CH_2Cl_2/MeOH/H_2O 70:10:1, flow rate 1.5 ml/min, r.t., detection at 225 nm): **3** (25.0 mg; t_R 31.2). *Peak 5* (t_R 100) was purified by prep. HPLC (*Cosmosil-5SL*, CH_2Cl_2/MeOH/H_2O 80:10:1, flow rate 1.5 ml/min, r.t., detection at 225 nm): **1** (8.5 mg; t_R 31.2) and **4** (30.5 mg; t_R 34.0). The BuOH-soluble fraction (9.7 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH/H_2O 30:10:1), and the eluate was separated into *Frs. 1–3*. *Fr. 1* was further subjected to CC (*Sephadex LH-20*, 50% MeOH), and the eluate was separated into *Frs. 1.1–1.5*. *Fr. 1.2* was subjected to prep. HPLC (*TSKgel-ODS-80TM*, MeOH/H_2O 1:3, flow rate 0.8 ml/min,

column temp. 40°, detection at 205 nm): **5** (3.0 mg; t_R 38.7) and **6** (6.5 mg; t_R 41.0). *Fr. 1.4* was subjected to prep. HPLC (*TSKgel-ODS-120T*, MeOH/H_2O 2:5, flow rate 1.5 ml/min, column temp. 40°, detection at 205 nm): **7** (4.8 mg; t_R 28.0), **8** (6.5 mg; t_R 31.0), **9** (7.0 mg; t_R 42.0), and **10** (12.5 mg; t_R 48.6).

7-O-Tigloylsecologanol (= rel-*(2*R*,3*S*,4*R*)-3-Ethenyl-2-(β-*D*-glucopyranosyloxy)-3,4-dihydro-4-{2-[(2-methyl-1-oxobut-2-en-1-yl)oxy]ethyl}-2*H*-pyran-5-carboxylic Acid Methyl Ester*; **1**): Amorphous powder. $[\alpha]_D^{27} = -70.0$ ($c = 0.20$, MeOH). UV (MeOH): 221 (4.07). ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. FAB-MS: 495 ($[M + Na]^+$). HR-FAB-MS: 495.1855 ($[M + Na]^+$, $C_{22}H_{32}NaO_{11}^+$; calc. 495.1829).

7-O-Tigloylsecologanolic Acid (= rel-*(2*R*,3*S*,4*R*)-3-Ethenyl-2-(β-*D*-glucopyranosyloxy)-3,4-dihydro-4-{2-[(2-methyl-1-oxobut-2-en-1-yl)oxy]ethyl}-2*H*-pyran-5-carboxylic Acid*; **2**): Amorphous powder. $[\alpha]_D^{27} = -116.2$ ($c = 0.37$, MeOH). UV (MeOH): 219 (4.18). ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. FAB-MS: 481 ($[M + Na]^+$). HR-FAB-MS: 481.1671 ($[M + Na]^+$, $C_{21}H_{30}NaO_{11}^+$; calc. 481.1686).

3′-O-[(2S)*-2-Methylbutanoyl]henryoside* (= *2″-(β-*D*-Glucopyranosyloxy)benzyl 2-Hydroxy-6-{[3-O-[*(2S)*-2-methylbutanoyl]-β-*D*-glucopyranosyl}oxy}benzoate* = *2-{{[2-[(β-*D*-Glucopyranosyl)oxy]phenyl}methoxy}carbonyl}-3-hydroxyphenyl β-*D*-Glucopyranoside 3-[(2S)-2-Methylbutanoate*; **3**): Amorphous powder. $[\alpha]_D^{27} = -43.5$ ($c = 0.23$, MeOH). UV (MeOH): 306 (3.24), 273 (3.39), 246 (3.67), 205 (4.38). ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 2*. FAB-MS: 691 ($[M + Na]^+$). HR-FAB-MS: 691.2207 ($[M + Na]^+$, $C_{31}H_{40}NaO_{16}^+$; calc. 691.2214).

Alkaline Hydrolysis and Determination of the Absolute Configuration of the 2-Methylbutanoyl Moiety in **3**. Compound **3** (5.0 mg) was treated with 5% KOH soln. (1.5 ml) for 1.5 h at 40°. The soln. was neutralized with 1M HCl and partitioned with $CHCl_3$. The $CHCl_3$ layer was dried (Na_2SO_4) and concentrated. The residue containing 2-methylbutanoic acid (**11**) was refluxed for 1 h with $SOCl_2$ (600 µl). The excess $SOCl_2$ was removed under reduced pressure to afford 2-methylbutanoyl chloride (**12**). Chloride **12** was dissolved in $CHCl_3$ (5 ml), and aniline (500 µl) was added dropwise. After stirring for 1.5 h at r.t., the $CHCl_3$ layer was washed three times with 4M HCl, dried (Na_2SO_4), and concentrated: amide **13**.

(2*S*)-2-Methyl-*N*-phenylbutanamide and racemic (2*RS*)-2-methyl-*N*-phenylbutanamide were synthesized from commercial (2*S*)-2-methylbutanoic acid and (2*RS*)-2-methylbutanoic acid by the method described above. The (2*R*)- and (2*S*)-enantiomers of 2-methyl-*N*-phenylbutanamide were separated by HPLC (*Daicel Chiral OD* (10 µm, 4.6 mm i.d. × 25 cm; *Daicel Chemical Co.*), column temp. r.t., hexane/i-PrOH 10:1, flow rate 0.5 ml/min, detection at 254 nm): **13**, t_R 24.0; (2*S*)-2-methyl-*N*-phenylbutanamide, t_R 24.0; (2*R*)-2-methyl-*N*-phenylbutanamide, t_R 26.4.

*(2*S*)-2-Methyl-*N*-phenylbutanamide:* Colorless crystals. $[\alpha]_D^{27} = +26.7$ ($c = 1.80$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (br. *d*, $J = 7.8$); 7.32 (*t*, $J = 7.8$); 7.10 (br. *t*, $J = 7.8$); 2.25 (*sext.*, $J = 7.3$); 1.78 (*dquint.*, $J = 15.1, 7.3$); 1.51 (*dquint.*, $J = 15.1, 7.3$); 1.24 (*d*, $J = 7.3$); 0.97 (*t*, $J = 7.3$). EI-MS: 177 (M^+). HR-EI-MS: 177.1154 (M^+, $C_{11}H_{15}NO^+$; calc. 177.1154).

Determination of the Absolute Configuration of the Sugar Residues in Compounds **1**–**3**. Each compound (*ca.* 1 mg) was refluxed with 1M HCl (1 ml) for 5 h. The mixture was neutralized with Ag_2CO_3 and filtered. The soln. was concentrated and dried to give a sugar fraction. The sugar fraction was analyzed by HPLC *TSKgel Amide-80* (10 µm, 7.8 mm i.d. × 30 cm; *Tosoh*), column temp. 45°, MeCN/H_2O 4:1, flow rate 1.0 ml/min, chiral detection (*Jasco OR-2090*). Identification of the D-glucose present in the sugar fraction was established by comparison of the t_R and $[\alpha]_D$ with that of an authentic sample; t_R 39.0 (D-glucose, pos. $[\alpha]_D$).

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