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(6*S*)-Hydroxy-3-oxo-α-ionol glucosides from *Capparis spinosa* fruits

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Abstract

Two new (6*S*)-hydroxy-3-oxo-α-ionol glucosides, together with corchoionoside C ((6*S*,9*S*)-roseoside) and a prenyl glucoside, were isolated from mature fruits of *Capparis spinosa*. The structures were established on the basis of spectroscopic, chiroptic and chemical evidence. In addition, the ^{13}C-resonance of C-9 was found to be of particular diagnostic value in assigning the absolute configuration at that center in ionol glycosides. The α-ionol derivatives are metabolites of (+)-(*S*)-abscisic acid.

Keywords: *Capparis spinosa*; Capparidaceae; (6*S*)-Hydroxy-3-oxo-α-ionol glucosides; Abscisic acid metabolites; ^{1}H NMR; ^{13}C NMR; CD spectra; Absolute configuration

1. Introduction

The genus *Capparis* (Capparidaceae) is represented by two species in the flora of Turkey (Davis, 1965). It is used in the traditional Turkish medicine for its diuretic, constipant and tonic properties (Baytop, 1999). In an earlier paper, we had reported on indole acetonitrile glycosides obtained from the methanolic extract of the mature fruits of *C. spinosa* (Çalış et al., 1999). In the course of a continuing study of this plant material, three (6*S*)-hydroxy-3-oxo-α-ionol glucosides (**1**–**3**)[1] and a prenyl glucoside (**5**) were isolated by chromatographic methods and their structures established by spectroscopic and chiroptic methods.

2. Results and discussion

Compound **1** was isolated as an amorphous colourless solid ($[\alpha]_D^{20}$ +31.2°). The UV spectrum of **1** (λ_{max} 234 nm) and the IR absorption (ν_{max} 1660 cm^{-1}) indicated the presence of an α,β-unsaturated ketone. Its molecular formula was established as $C_{19}H_{30}O_8$ from the ESIMS (*m*/*z* 409 $[M+Na]^+$ and 795 $[2M+Na]^+$) and NMR data. The ^{1}H and ^{13}C NMR spectra (Table 1) of **1**, which were assigned by 2D experiments (COSY, HSQC and HMBC), showed the presence of a β-glucopyranosyl unit and an aglycone moiety consisting of 13 carbon atoms. Of the signals attributed to the aglycone, a disubstituted (*E*)-olefin (δ_H 5.94 *d*, *J* = 15.5 Hz; 5.64 *dd*, *J* = 15.5 and 6.4 Hz), an oxymethine proton (δ_H 4.43 *dq*, *J* = 6.4 and 6.5 Hz) and a secondary methyl group (δ_H 1.19 *d*, *J* = 6.5 Hz) were observed as an AMXY$_3$-type spin system. Additional signals were due to three tertiary methyl groups, one being vinylic (δ_H 1.82 *d*, *J* = 1.1 Hz), a vinyl proton (δ_H 5.76 br. *s*) and a carbonyl group (δ_C 197.2). These spectroscopic data suggested that **1** has basically the same skeleton as roseoside ((+)-(6*S*,9*R*)-9-*O*-β-D-glucopyranosyloxy-6-hydroxy-3-oxo-α-ionol) which was first isolated from *Vinca rosea* (Bhakuni et al., 1974). Later, roseoside was shown to be a constituent of various plant species but some conflicting physical data have been reported for the compound from different sources (see the comprehensive discussion of the stereochemical implications by Otsuka et al., 1995). Compared to the ^{13}C NMR spectral data of (6*S*,9*R*)-roseoside (Otsuka et al., 1995; Yoshikawa et al., 1997), the chemical shift values assigned to C-7, C-8, and C-9 in **1** (δ_C 131.6, 131.4, and 71.9) were significantly different. But they were similar to those reported for corchoionoside C from *Corchorus olitorius* which is the (9*S*)-

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[1] The atom numbering follows the systematics of the carotenoids.

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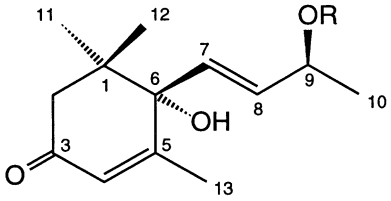
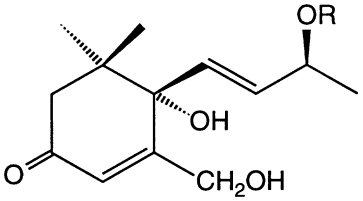


1 R = β-D-glucose
1a R = β-D-glucose $(OAc)_4$
1b R = H
1c R = (*R*)-MTPA
1d R = (*S*)-MTPA



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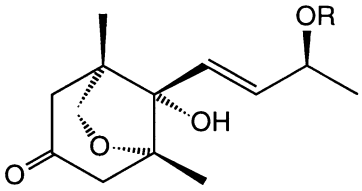
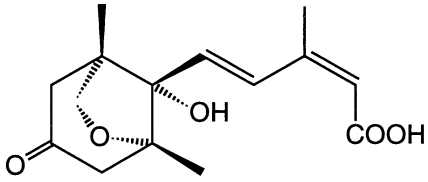
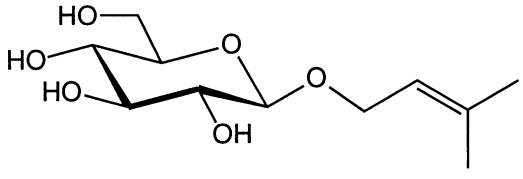




3 R = β-D-glucose
3a R = β-D-glucose $(OAc)_4$
3b R = H
3c R = (*R*)-MTPA
3d R = (*S*)-MTPA

4



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epimer of roseoside (Yoshikawa, et al., 1997) and has also a similar positive optical rotation ($[\alpha]_D^{22}$ +25.3°).

For a further evaluation **1** was acetylated yielding the tetraacetate **1a**. The ^{1}H NMR spectroscopic data of **1a** (Table 1) were identical to those of roseoside tetraacetate reported by Achenbach et al. (1981) and Baltenweck-Guyot et al. (1996). Moreover, **1** was subjected to enzymatic hydrolysis by β-glucosidase (emulsin) yielding the aglycone **1b** and D-glucose. The ^{1}H NMR spectroscopic data of **1b** (Table 1) were identical to those reported by Gonzáles et al. (1994) for blumenol A which has (6*S*,9*R*)-chirality (Galbraith and Horn, 1973; Weiss et al., 1973). Several inconsistencies of data and nomenclature in the currrent literature prompted us to establish the

Table 1
NMR spectroscopic data for **1**, **1a** and **1b** (^{1}H: 600 MHz; ^{13}C: 150 MHz)

	1 (DMSO-d_6)			**1a** ($CDCl_3$)	**1b** ($CDCl_3$)
C/H atom	δ_C	DEPT	δ_H ppm, J (Hz)	δ_H ppm, J (Hz)	δ_H ppm, J (Hz)
1	40.9	C	–	–	–
2	49.3	CH_2	2.54 *d* (16.6)	2.45 *d* (17.0)	2.45 *d* (17.0)
			2.05 *d* (16.6)	2.28 *d* (17.0)	2.24 *d* (17.0)
3	197.2	C	–	–	–
4	125.5	CH	5.76 br *s*	5.93 br *s*	5.90 br *s*
5	163.6	C	–	–	–
6	77.9	C	–	–	–
7	131.6	CH	5.94 *d* (15.5)	5.75 *d* (15.6)	5.79 *d* (15.7)
8	131.4	CH	5.64 *dd* (15.5, 6.4)	5.68 *dd* (15.6, 6.2)	5.88 *ddd* (15.7, 5.8)
9	71.9	CH	4.43 *dq* (6.4, 6.5)	4.36 *dq* (6.2, 6.4)	4.41 *dq* (6.4, 5.8)
10	22.0	CH_3	1.19 *d* (6.5)	1.30 *d* (6.4)	1.30 *d* (6.4)
11	23.1	CH_3	0.93 *s*	1.09 *s*	1.08
12	24.1	CH_3	0.92 *s*	1.00 *s*	1.00
13	18.6	CH_3	1.82 *d* (1.1)	1.93 br *s*	1.90 *d* (1.3)
6-OH	–	–	4.98 *s*	4.80 *s*	
1′	99.9	CH	4.09 *d* (7.8)	4.50 *d* (7.9)	
2′	73.3	CH	2.95	4.98 *dd* (7.9, 9.2)	
3′	77.0	CH	3.04	5.16 *t* (9.2)	
4′	70.0	CH	3.01	5.07 *t* (9.5)	
5′	77.1	CH	2.93	3.62 *ddd* (9.5, 4.6, 2.4)	
6′	61.0	CH_2	3.64 *m*, 3.41 *m*	4.25 *dd* (12.3, 4.6)	
				4.13 *dd* (12.3, 2.4)	
				2.08, 2.02, 2.01, 2.00 all *s*, 3H (aliph. acetoxyl)	

absolute configuration of the aglycone unambiguously by the high-field ^{1}H NMR Mosher method (Ohtani et al., 1991). Therefore, **1b** was treated with (*R*)- and (*S*)-α-methoxy-α-trifluoromethyl-phenylacetic acid (MTPA) to yield the corresponding MTPA-esters **1c** (9-(*R*)-MTPA) and **1d** (9-(*S*)-MTPA). According to the values of $\Delta\delta = [\delta(S\text{-MTPA ester}) - \delta(R\text{-MTPA ester})]$ of the protons at C-7, C-8, C-9, and C-10 in **1c** and **1d** (see Experimental), the (9*S*)-configuration was unequivocally assigned for **1b**. As a consequence of this result, it can be stated that the ^{13}C-resonance of C-9 is of particular diagnostic value in assigning the absolute configuration at C-9 in ionol glycosides such as **1**. Hence, an upfield shift of C-9 (ca. 74 ppm) is indicative for the (9*S*)-configuration whereas compounds with (9*R*)-configuration exhibit a lower field signal (ca. 77 ppm). This empirical rule could be verified by thorough comparison with literature data. A similar finding concerning relative displacements of the C-10 resonances was reported by Pabst et al. (1992) for diastereomeric 3-oxo-α-ionol glucosides.

The (6*S*)-configuration, as found in natural (+)-abscisic acid (Ryback, 1972; Harada, 1973; Koreeda et al., 1973) was deduced from the CD spectra of either the genuine compound **1** ($\Delta\varepsilon_{237}$ +31.3, $\Delta\varepsilon_{318}$−2.5) and its aglycone **1b** ($\Delta\varepsilon_{242}$ +4.1, $\Delta\varepsilon_{307}$−1.4) which were superimposable to those reported. As a consequence, compound **1** is (+)-(6*S*,9*S*)-9-*O*-β-D-glucopyranosyloxy-6-hydroxy-3-oxo-α-ionol (corchoionoside C, (6*S*,9*S*)-roseoside).

Constituent **2** was obtained as an amorphous colourless solid ($[\alpha]_D^{20}$ −43.0°). The UV spectrum of **2** (λ_{max} 235 nm) and its IR absorption (ν_{max} 1653 cm^{-1}) indicated the presence of an α,β-unsaturated ketone as in **1**. The elemental composition was determined to be $C_{19}H_{30}O_9$ from the ESIMS (*m*/*z* 425 $[M+Na]^+$) and NMR data. Of the 19 carbon signals observed in the ^{13}C NMR spectrum (Table 2), six were attributed to a β-glucopyranosyl unit. The remaining signals were consistent for the presence of three methyl, two methylene, five methine and three quaternary carbons. The main difference between **1** and **2** was the oxymethylene functionality for **2**, instead of the vinylic methyl signal in **1**. This observation was also supported by the ESIMS showing 16 mass units higher for **2**. In the ^{1}H NMR spectrum three methyl signals, two being singlets (δ 0.89 and 0.91) and one doublet (δ_H 1.16, J = 6.4 Hz), were observed. The oxymethylene group was evident from the ^{1}H (δ_H 4.23 and 4.00, J_{AB} = 18.6 Hz, H_2-13) and the corresponding ^{13}C NMR resonances (δ 59.1, C-13). An olefinic proton at the α-carbon of an α,β-unsaturated ketone (δ_H 5.96 br. *s*, H-4), two (*E*)-oriented vinyl protons (δ_H 5.93 *d*, J = 15.6 Hz and 5.57 *dd*, J = 15.6 and 6.2 Hz, H-7 and H-8, respectively), one methylene (δ_H 2.48 and 2.08, AB system, J_{AB} = 16.4 Hz, H_2-2) and one oxymethine (δ_H 4.40 *dq*, J = 6.4 and 6.2 Hz, H-9) protons were the other signals observed. All the assignments are based on a series of 2D NMR experiments (COSY, HSQC and HMBC). The HMBC correlations from the

Table 2
^{1}H and ^{13}C NMR spectroscopic data for **2** (^{1}H: 600 MHz; ^{13}C: 150 MHz)

	2 (DMSO-d_6)			
C/H atom	δ_C	DEPT	δ_H ppm, J (Hz)	HMBC
1	41.3	C	–	Me-11, Me-12
2	49.3	CH_2	2.48 *d* (16.4) 2.08 *d* (16.4)	Me-11, Me-12
3	197.2	C	–	H_2-2
4	121.2	CH	5.96 br. *s*	H_2-13
5	167.0	C	–	H_2-13
6	77.1	C	–	H-7, H-8, Me-11, Me-12
7	131.6	CH	5.93 *d* (15.6)	H-9
8	131.3	CH	5.57 *dd* (15.6, 6.2)	H-9, Me-10
9	72.0	CH	4.40 *dq* (6.4, 6.2)	H-7, H-8, Me-10, H-1′
10	22.1	CH_3	1.16 *d* (6.4)	H-9
11	23.6	CH_3	0.91 *s*	Me-12, H_2-2
12	23.0	CH_3	0.89 *s*	Me-11, H_2-2
13	59.1	CH_2	4.23 *d* (18.6) 4.00 *d* (18.6)	H-4
6-OH	–	–	4.98 *s*	
1′	100.0	CH	4.07 *d* (7.7)	H-9
2′	73.3	CH	2.95[a]	
3′	76.9	CH	3.05[a]	
4′	70.0	CH	3.02[a]	
5′	77.1	CH	2.98[a]	
6′	61.1	CH_2	3.63 br *d* (12.0) 3.42 *dd* (12.0, 4.5)	

[a] Signal patterns are not clear due to overlapping.

oxymethylene protons to C-5 (δ_C 167.0) as well as to C-4 (δ_C 121.2) located the hydroxymethyl group (C-13) at C-5. The NMR data were almost identical to those of inamoside, a 13-hydroxy-3-oxo-α-ionone glucoside from *Ophiorrhiza pumila* (Aimi et al., 1990) hence, the gross structure of **2** could be assigned as a 6,13-dihydroxy-3-oxo-α-ionol glucoside. As the observed CD data ($\Delta\varepsilon_{241}$ +6.9, $\Delta\varepsilon_{315}$−1.8) agreed well with those of inamoside and that of **1** and **1b**, the (*S*)-configuration at C-6 was deduced. The upfield shift of C-9 (72.0 ppm), as well as the supposed biogenetic relationship with **1** indicate the absolute configuration at C-9 to be (*S*). Thus, the structure of **2** was determined as (6*S*,9*S*)-6-hydroxyinamoside ((−)-(6*S*,9*S*)-9-*O*-β-D-glucopyranosyloxy-6,13-dihydroxy-3-oxo-α-ionol) and spionoside A is proposed as trivial name.

Compound **3** was isolated as an amorphous colourless solid ($[\alpha]_D^{20}$ −51.2°). From the ESIMS (*m*/*z* 425 [M+Na]+) and NMR data its molecular formula was determined to be $C_{19}H_{30}O_9$ thus identical with that of **2**. The NMR spectra (Table 3) showed a β-glucopyranoside (δ_H 4.12 *d*, J=7.3 Hz; δ_C 100.0) and an aglycone part consisting of a ring-modified 3-oxo-ionol moiety. The signals from the side chain (H-7 to Me-10) gave rise to the same spin sytem as in **1** and **2** in the ^{1}H NMR. The diagnostic most relevant feature was an oxymethylene group at C-11 (δ_H 3.72, *dd*, J=7.5, and 2.3 Hz, 3.48, J=7.5 Hz; δ_C 76.8) that exhibited HMBC correlations with C-1, C-5 and C-6, implying a tetrahydrofuran moiety. This assumption was corroborated by the characteristic value of the geminal coupling constant (Cookson et al., 1966). Moreover, a ketone function (δ_C 209.0) showed long-range correlations to both methylene groups assigned as H_2-2 and H_2-4 as well as to Me-12 and Me-13. The proposed constitution for the aglycone of **3** was identical with drummondol (Powell et al., 1981, 1986). In order to verify this assumption, **3** was acetylated yielding the tetraacetate **3a** (ESIMS *m*/*z* 593 [M+Na]+, corresponding to $C_{27}H_{38}O_{13}$) that exhibited the expected signal pattern (Table 3).

Enzymatic hydrolysis of **3** by emulsin yielded the aglycone **3b** and D-glucose. The ^{1}H NMR spectrum of **3b** exhibited signals which were superimposable to those of drummondol reported by Powell et al. (1981, 1986). As the absolute configuration at C-9 of drummondol remained undetermined, we established it by analyzing the corresponding MTPA-derivatives **3c** (9-(*R*)-MTPA) and **3d** (9-(*S*)-MTPA). According to the values of $\Delta\delta$ in the ^{1}H NMR spectra (see Experimental), the (9*S*)-configuration of **3b**, and, as a consequence, for the genuine glucoside **3** was assigned. In addition, the upfield shift of C-9 (72.3 ppm) in **3** again demonstrates its significance.

Finally, the Cotton effects in the CD spectrum of **3** ($\Delta\varepsilon_{244}$+2.3, $\Delta\varepsilon_{296}$−2.3) and **3a** ($\Delta\varepsilon_{245}$+0.9, $\Delta\varepsilon_{297}$−1.7) showed the same signs as expected for the related (+)-(*S*)-abscisic acid metabolites. Hence, the (6*S*)-configuration can be assigned as determined for phaseic acid (**4**) on the basis of NMR and IR spectroscopic arguments (Mill-

Table 3
NMR spectroscopic data for **3**, **3a** and **3b** (^{1}H: 600 MHz; ^{13}C: 150 MHz)

	3 (DMSO-d_6)			**3a** ($CDCl_3$)[a]		**3b** ($CDCl_3$)
C/H atom	δ_C	DEPT	δ_H ppm, *J* (Hz)	δ_C	δ_H ppm, *J* (Hz)	δ_H ppm, *J* (Hz)
1	48.0	C	–	47.7	–	–
2	52.1	CH_2	2.63 *dd* (17.7, 2.3) 2.21 *dd* (17.7, 2.3)	52.4	2.54 *dd* (18.4, 2.6) 2.45 *dd* (18.4, 2.0)	2.55 *dd* (18.4, 2.7) 2.41 *dd* (18.4, 2.7)
3	209.0	C	–	207.7	–	–
4	53.2	CH_2	2.70 *d* (17.7) 2.27 *dd* (17.7, 2.3)	52.5	2.66 *dd* (18.4, 2.0) 2.60 *d* (18.4)	2.62 br *s*
5	86.1	C	–	85.4	–	–
6	81.1	C	–	81.7	–	–
7	128.0	CH	6.21 *d* (15.5)	126.8	5.85 *d* (15.3)	5.91 *dd* (15.3, 1.4)
8	135.3	CH	5.88 *dd* (15.5, 6.4)	136.5	6.03 *dd* (15.3, 6.6)	6.23 *dd* (15.3, 5.3)
9	72.3	CH	4.48 *dq* (6.4, 6.5)	75.4	4.39 *dq* (6.6, 6.5)	4.45 *dq* (5.3, 6.5)
10	22.5	CH_3	1.20 *d* (6.5)	22.1	1.35 *d* (6.5)	1.33 *d* (6.5)
11	76.8	CH_2	3.72 *dd* (7.5, 2.3) 3.48 *d* (7.5)	77.2	3.91 *ddd* (8.4, 2.8) 3.78 *d* (8.4)	3.90 *dd* (8.2, 2.8) 3.75 *d* (8.2)
12	15.5	CH_3	0.82 *s*	15.7	0.99 *s*	0.99 *s*
13	19.4	CH_3	1.05 *s*	18.8	1.23 *s*	1.20 *s*
6-OH	–	–	4.80 *s*			
1′	100.0	CH	4.12 *d* (7.3)	98.6	4.57 *d* (7.9)	
2′	73.5	CH	2.95[b]	71.7	4.88 *dd* (7.9, 9.5)	
3′	77.0	CH	3.05 *t* (9.0)	72.7	5.19 *t* (9.5)	
4′	70.4	CH	2.99 *t* (9.0)	68.4	5.08 *t* (9.5)	
5′	77.3	CH	2.97[b]	71.8	3.65 *m*	
6′	61.3	CH_2	3.63[b] 3.38 *dd* (11.8, 5.0)	62.1	4.26 *dd* (12.3, 5.0) 4.14 *dd* (12.3, 2.5)	

[a] Additional signals for **3a**: δ_C 170.7, 170.3, 169.4, 169.3 (all C), 20.8, 20.7, 20.6 (×2) (all CH_3); δ_H 2.09, 2.03, 2.02, 2.01 (all 3H, *s*).
[b] Signal patterns are not clear due to overlapping.

borrow, 1975). However, a direct chiroptical correlation was precluded due to lacking CD data in the current literature. Therefore, the structure of compound **3** was determined as (9*S*)-drummondol-9-*O*-β-D-glucopyranoside, for which spionoside B is proposed as trivial name.

Compound **5** was isolated as an amorphous powder ($[\alpha]_D^{20}$ −23.0°) and identified as (−)-1-*O*-β-D-glucopyranosyloxy-3-methyl-2-buten-1-ol (Kitajima, 1998). This is only the 3rd account on the isolation of this compound from natural sources, the 1st being reported not earlier than 1996 (Yoshikawa et al., 1996).

3. Experimental

3.1. General

As reported in the previous study (Çalış et al., 1999).

3.2. Plant material

Mature fruits of *C. spinosa* L. were collected from Mut, İçel, Turkey in September 1993. A voucher specimen has been deposited in the herbarium of the Faculty of Pharmacy, Hacettepe University, Ankara, Turkey (HUEF 94008).

3.3. Extraction and isolation

Mature fruits of *C. spinosa* L. were stored frozen at −20 °C. Freeze-dried (1.2 kg) and sliced plant material was homogenized in MeOH (2×2.5 l) and kept overnight at room temperature. The combined MeOH extracts were concentrated to dryness in vacuo. The water soluble part of the MeOH extract was fractionated by vacuum liquid column chromatography (VLC) on LiChroprep RP-18 (Merck) using a H_2O–MeOH gradient. After separation of the indol-3-acetonitrile glycosides, capparillosides A and B, from the fractions eluting with 50% MeOH (Çalış et al., 1999), the remaining fractions were purified by repeated Si gel column chromatographies eluting with $CHCl_3$–MeOH–H_2O (90:10:1–70:30:3) and EtOAc–MeOH (100:0–100:10) to give compounds **3** (15 mg), **5** (55 mg), **1** (34 mg) and **2** (10 mg), respectively.

3.4. Corchoionoside C (*1*) ((+)-(6S,9S)-9-O-β-D-glucopyranosyloxy-6-hydroxy-3-oxo-α-ionol, (6S,9S)-roseoside))

Amorphous. $[\alpha]_D^{20}$ +31.2° (*c* 2.0, MeOH). ESIMS *m/z* 409 $[M+Na]^+$ and 795 $[2M+Na]^+$ (calc. for $C_{19}H_{30}O_8$). UV λ_{max} (MeOH): 234 nm. CD $\Delta\varepsilon_{237}$ +31.3, $\Delta\varepsilon_{319}$−2.35 (MeOH, *c* 7.8×10^{-5} M). IR υ_{max} (KBr):

3407 (OH), 2930 (CH), 1660 (enone), 1075, 1040 cm^{-1}(C–O–C). ^1H and ^{13}C NMR (DMSO-d_6): Table 1.

3.5. Spionoside A (2) ((6S,9S)-6-hydroxyinamoside, ((−)-(6S,9S)-9-O-β-D-glucopyranosyloxy-6,13-dihydroxy-3-oxo-α-ionol))

Amorphous. $[\alpha]_D^{20}$ −43.0° (*c* 0.3, MeOH). ESIMS *m/z* 425 $[M+Na]^+$ (calc. for $C_{19}H_{30}O_9$). UV λ_{max} (MeOH): 245 nm. CD $\Delta\varepsilon_{241}$ +6.9, $\Delta\varepsilon_{315}$−1.8 (MeOH, *c* 8.9×10^{-5} M). IR υ_{max} (KBr): 3400 (OH), 2930 (CH), 1653 (enone), 1040 cm^{-1}(C–O–C). ^1H and ^{13}C NMR (DMSO-d_6): Table 2.

3.6. Spionoside B (3) ((9S)-drummondol-9-O-β-D-glucopyranoside))

Amorphous. $[\alpha]_D^{20}$ −51.2° (*c* 2.0, MeOH). ESIMS *m/z* 425 $[M+Na]+$ (calc. for $C_{19}H_{30}O_9$). UV λ_{max} (MeOH): 209 nm. CD $\Delta\varepsilon_{244}$ +2.3, $\Delta\varepsilon_{296}$−2.3 (MeOH, *c* 1.0×10^{-4} M). IR υ_{max} (KBr): 3450 (OH), 2925 (CH), 1045 cm^{-1}(C–O–C). ^1H and ^{13}C NMR (DMSO-d_6): Table 3.

3.7. Acetylation of 1 and 3

Compounds **1** and **3** (each 5 mg) were separately treated with Ac_2O and pyridine (each 0.5 ml) at room temp. overnight. The reaction mixtures were diluted with H_2O (2 ml), adsorbed on an RP-18 cartridge (Waters, Sep-Pak®Vak) and thoroughly washed with H_2O. Elution with $CHCl_3$ yielded the acetates **1a** and **3a**, respectively. ^1H NMR ($CDCl_3$): see Tables 1 and 3, respectively.

3.8. Enzymatic hydrolysis of 1 and 3

The solutions of **1** and **3** (each 10 mg) in acetate buffer (pH 4.4, 10 ml) were treated separately with β-glucosidase (15 mg), and the solutions were left at 37 °C for 48 h. The reaction solutions were evaporated to dryness, and the residues were separately chromatographed on silica gel (7 g), using CH_2Cl_2–MeOH–H_2O (90:10:1) to afford **1a** ((9*S*)-blumenol A, 5 mg) and **3a** ((9*S*)-drummondol, 5 mg), respectively. ^1H NMR ($CDCl_3$): Tables 1 and 3, respectively. CD of **1b** $\Delta\varepsilon_{242}$ +4.1, $\Delta\varepsilon_{307}$−1.4 (MeOH, *c* 1.3×10^{-4} M). CD of **3a** $\Delta\varepsilon_{245}$ +0.9, $\Delta\varepsilon_{297}$−21.7 (MeOH, *c* 8.3×10^{-5} M).

3.9. (R)- and (S)-MTPA esters of 1 and 3

The solutions of the respective aglycones **1** and **3** (each 2.5 mg) in CH_2Cl_2 (1.5 ml) were treated separately with (*R*)- and (*S*)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) (25 mg) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (21 mg) and 4-dimethylaminopyridine (13 mg). The mixtures were kept at room temperature over night, then poured into ice-water and extracted with Et_2O. After work-up the residues were purified by prep. TLC (silica gel, hexane–acetone 2:1, R_f ca. 0.3) to yield the MTPA-esters **1c**, **1d** and **3c**, **3d**, respectively (each ca. 2 mg).

^1H NMR ($CDCl_3$, 600 MHz) of **1d** ((*R*)-MTPA ester): δ 0.92 (*s*, Me-12), 1.04 (*s*, Me-11), 1.44 (*d*, *J* = 6.5, Me-10), 1.82 (*d*, *J* = 1.4, Me-13), 2.19, 2.28 (AB, *J* = 17, H_2-2), 3.56 (*q*, *J* = 1.2, OMe), 5.65 (*quint*.-like, *J* ≈ 6.5, H-9), 5.76 (*m*, H-7, H-8), 5.88 (*q*, *J* = 1.4, H-4), 7.35–7.42 (3H), 7.49-7.52 (2H) (*m*, ar-H).

^1H NMR ($CDCl_3$, 600 MHz) of **1d** ((*S*)-MTPA ester): δ 0.97 (*s*, Me-12), 1.07 (*s*, Me-11), 1.40 (*d*, *J* = 6.5, Me-10), 1.84 (*d*, *J* = 1.3, Me-13), 2.23, 2.34 (AB, *J* = 17, H_2-2), 3.51 (*q*, *J* < 1, OMe), 5.63 (*dq*, *J* = 6.5, 6.2, H-9), 5.87 (*m*, H-7, H-8), 5.91 (*q*, *J* = 1.3, H-4), 7.36–7.42 (3H), 7.49–7.52 (2H) (*m*, ar-H).

^1H NMR ($CDCl_3$, 600 MHz) of **3c** ((*R*)-MTPA ester): δ 0.94 (*s*, Me-12), 1.12 (*s*, Me-13), 1.48 (*d*, *J* = 6.6, Me-10), 2.34, 2.37 (AB, *J* = 19.8, H_2-4), 2,48 (*d*, *J* = 18.2, H_a-2), 2.56 (*dd*, *J* = 18.2, 1.5, H_b-2), 3.55 (*q*, *J* < 1, OMe), 3.74 (*d*, *J* = 8.4, H_a-11), 3.86 (*dd*, *J* = 8.4, 1.5, H_b-11), 5.68 (*dq*, *J* = 6.6, 6.0, H-9), 5.88 (*d*, *J* = 15.2, H-7), 6.12 (*dd*, *J* = 15.2, 6.0, H-8), 7.36–7.43 (3H), 7.49–7.52 (2H) (*m*, ar-H).

^1H NMR ($CDCl_3$, 600 MHz) of **3d** ((*S*)-MTPA ester): δ 0.97 (*s*, Me-12), 1.19 (*s*, Me-13), 1.44 (*d*, *J* = 6.5, Me-10), 2.34, 2.43 (AB, *J* = 19.8, H_2-4), 2.52 (*d*, *J* = 18.2, H_a-2), 2.58 (*dd*, *J* = 18.2, 1.2, H_b-2), 3.51 (*q*, *J* < 1, OMe), 3.74 (*d*, *J* = 8.4, H_a-11), 3.88 (*dd*, *J* = 8.4, 2.0, H_b-11), 5.65 (*quint*., *J* = 6.5 H-9), 6.00 (*d*, *J* = 15.2, H-7), 6.19 (*dd*, *J* = 15.2, 6.5, H-8), 7.35–7.43 (3H), 7.49–7.52 (2H) (*m*, ar-H).

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