Structural Revisions of Blumenol C Glucoside and Byzantionoside B

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The absolute stereochemistry of blumenol C glucoside and byzantionoside B was revised here as (6*R*,9*S*)- and (6*R*,9*R*)-9-hydroxymegastigman-4-en-3-one 9-*O*-β-D-glucopyranosides, respectively, by modified Mosher's method. The empirical rules of ¹³C-NMR chemical shift to determine the absolute stereochemistry of C-9 of 9-hydroxymegastigmane 9-*O*-β-D-glucopyranoside were also discussed.

Key words blumenol C glucoside; byzantionoside B; megastigmane glucoside

Blumenol C was first isolated from the leaves of *Podocarpus blumei* in 1972.¹⁾ The absolute stereochemistry of blumenol C was then determined as (6*R*,9*R*) by chemical conversion of related compound.²⁾ Its glucoside, *i.e.* blumenol C glucoside (**1**), was then isolated from the aerial parts of *Epimedium grandiflorum* var. *thunbergianum* and the structure was determined by comparison of the spectral data of its aglycone, derived from enzymatic hydrolysis of **1**, with those of blumenol C.³⁾ Recently, byzantionoside B (**2**) was isolated from the aerial parts of *Stachys byzantina* as the C-9 epimer of blumenol C glucoside.⁴⁾ Modified Mosher's method is widely used recently for determination of the absolute stereochemistry of chiral secondary alcohol.⁵⁾ In this study, the absolute configurations of these compounds (**1**, **2**) were reinvestigated by this reliable method.

Results and Discussion

Blumenol C glucoside (**1**) and byzantionoside B (**2**) were identified by comparison of the literature data at first (Tables 1, 2).^{3,4)} The aglycones (**1a**, **2a**, respectively) were prepared by enzymatic hydrolysis of the glucosides. Their (*R*)- or (*S*)-MTPA esters were then prepared by the conventional procedure (**1b** and **1c** from **1a**, **2b** and **2c** from **2a**, see Experimental). The distribution patterns of $\Delta\delta_{S-R}$ values for **1b** and **1c**, and **2b** and **2c** clearly demonstrated that **1** and **2** possess 9*S* and 9*R* configurations, respectively (Figs. 1, 2). In addition, the application of the β-D-glucosylation-induced shift-trend rule⁶⁾ also supported this result (Table 1). The absolute stereochemistry of C-6 was also confirmed by CD spectra. The CD data of **1** and **2** were essentially identical to that of sedumoside H of which the absolute stereochemistry was determined precisely by catalytic hydrogenation and application of CD octant rule, and also chemical conversion to related compound.^{7,8)} Therefore, the actual structures of **1** and **2** must be (6*R*,9*S*)-9-hydroxymegastigman-4-en-3-one 9-*O*-β-D-glucopyranoside and (6*R*,9*R*)-9-hydroxymegastigman-4-en-3-one 9-*O*-β-D-glucopyranoside, respectively (Fig. 1).

Fig. 1. Revised Structures of Blumenol C Glucoside (**1**) and Byzantionoside B (**2**)

Fig. 2. Modified Mosher's Analysis for **1** and **2**

Thus, blumenol C glucoside (**1**) isn't the glucoside of blumenol C, but the glucoside of 9-*epi*-blumenol C in fact, and in other word, byzantionoside B is the really glucoside of blumenol C.

Aasen *et al.* reported the specific optical rotation value of blumenol C as $[\alpha]_D^{25} +54^\circ$ ($c=0.22$, CHCl_3).²⁾ Thus, blumenol C glucoside (**1**) was first misidentified as a glucoside of blumenol C, probably due to the moderate positive optical rotation value of aglycone $[[\alpha]_D^{22} +112.5^\circ$ ($c=0.52$, CHCl_3)].³⁾ However, the aglycones (**1a**, **2a**) prepared in this study from blumenol C glucoside (**1**) and byzantionoside B (**2**) showed $[\alpha]_D^{24} +80.5^\circ$ ($c=0.32$, CHCl_3) and $[\alpha]_D^{23} +46.3^\circ$ ($c=0.08$, CHCl_3), respectively, suggesting that it was difficult to distinguish these epimers only by optical rotation values at that time. Finally, it is noteworthy that there is a slight but clear difference between 9-*epi*-blumenol C (**1a**) and blumenol C (**2a**) for H₂-7 in ¹H-NMR spectra, *i.e.* 1.61 and 1.76 ppm for **1a**, and 1.45 and 1.93 ppm for **2a**. The comparison of chemical shifts of H₂-7 also provides the important criterion to distinguish each other (Table 2).

The above results arouse further interest that whether or not there was some trend in NMR spectra between (9*R*) and (9*S*)-*O*-β-D-glucopyranosides among related megastigmanes. It has been reported that the chemical shift at C-9 is indicative for 9*R* (*ca.* 77 ppm) and 9*S* (*ca.* 74 ppm) configuration for Δ^{7,8}-type of 9-hydroxymegastigmane 9-*O*-β-D-glucopyranoside.^{9,10)} This rule seems to be applicable for most compounds, however, in the case of staphylinoside I (δ_{C-9} : 76.3 ppm, 9*S*) that possessed 6-OMe, this rule does not work well for the determination of C-9 configuration.¹¹⁾ Therefore, in this paper, this rule was also refined further by comparing with the literature data (Fig. 3). The stereochemistry of these compounds was determined by the reliable methods, *i.e.* modified Mosher's method, β-D-glucosylation-induced shift-trend rule, synthetic approach and chemical conversion.

The empirical rules observed here are as follows: The

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Table 1. ^{13}C -NMR Data for Blumenol C Glucoside (**1**) and Byzantionoside B (**2**) (150 MHz)

C	1 ($\text{C}_5\text{D}_5\text{N}$)	1 (CD_3OD)	1a (CD_3OD)	2 ($\text{C}_5\text{D}_5\text{N}$)	2 (CD_3OD)	2a (CD_3OD)
1	36.4	37.4	37.4	36.3	37.4	37.4
2	47.8	48.2	48.3	47.8	48.2	48.2
3	198.4	202.4	202.2	198.4	202.5	202.3
4	125.4	125.6	125.6	125.4	125.5	125.5
5	165.2	169.8	169.7	165.2	170.1	169.7
6	51.3	52.7	52.6	51.2	52.5	52.5
7	25.7	26.7	27.5	26.0	26.9	27.3
8	36.7	37.5	39.9(−2.4)	37.1	37.9	39.9(−2.0)
9	76.0	77.7	68.9(+8.8)	74.2	75.7	68.6(+7.1)
10	22.0	22.0	23.5(−1.5)	19.9	19.9	23.6(−3.7)
11	28.7	29.1	29.1	28.8	29.1	29.1
12	27.1	27.5	27.4	27.1	27.6	27.5
13	24.3	25.0	24.9	24.3	25.0	24.8
1'	104.2	104.1		102.4	102.3	
2'	75.4	75.4		75.3	75.3	
3'	78.7	78.3		78.7	78.3	
4'	71.9	71.8		72.1	72.0	
5'	78.4	77.9		78.4	78.0	
6'	63.0	62.9		63.2	63.1	

Parenthesis is $\delta_{\text{glucoside-aglycone}}$.

Table 2. ^1H -NMR Data for Blumenol C Glucoside (**1**) and Byzantionoside B (**2**) (600 MHz)

C	1 ($\text{C}_5\text{D}_5\text{N}$)	1 (CD_3OD)	1a (CD_3OD)	2 ($\text{C}_5\text{D}_5\text{N}$)	2 (CD_3OD)	2a (CD_3OD)
2	2.08 (1H, d, 17)	1.98 (1H, d, 17)	2.00 (1H, d, 17)	2.07 (1H, d, 17)	1.97 (1H, d, 17)	1.99 (1H, m)
	2.49 (1H, d, 17)	2.48 (1H, d, 17)	2.44 (1H, d, 17)	2.45 (1H, d, 17)	2.46 (1H, d, 17)	2.44 (1H, d, 17)
4	5.89 (1H, s)	5.80 (1H, s)	5.81 (1H, s)	5.92 (1H, m)	5.80 (1H, s)	5.81 (1H, s)
6	1.78 (1H, m)	1.97 (1H, m)	1.99 (1H, m)	1.77 (1H, m)	1.99 (1H, m)	1.98 (1H, m)
7	1.75—1.89 (2H, m)	1.67 (1H, m)	1.61 (1H, m)	1.50 (1H, m)	1.50 (1H, m)	1.45 (1H, m)
		1.81 (1H, m)	1.76 (1H, m)	1.94 (1H, m)	1.98 (1H, m)	1.93 (1H, m)
8	1.66—1.77 (2H, m)	1.61 (1H, m)	1.51—1.56 (2H, m)	1.62 (1H, m)	1.61 (1H, m)	1.51—1.55 (2H, m)
		1.68 (1H, m)		1.76 (1H, m)	1.68 (1H, m)	
9	4.04 (1H, m)	3.82 (1H, m)	3.69 (1H, m)	4.06 (1H, m)	3.88 (1H, m)	3.69 (1H, m)
10	1.37 (3H, d, 6)	1.25 (3H, d, 6)	1.16 (3H, d, 6)	1.27 (3H, d, 6)	1.18 (3H, d, 6)	1.16 (3H, d, 6)
11	0.93 (3H, s)	1.02 (3H, s)	1.02 (3H, s)	0.92 (3H, s)	1.01 (3H, s)	1.02 (3H, s)
12	0.98 (3H, s)	1.09 (3H, s)	1.09 (3H, s)	0.94 (3H, s)	1.09 (3H, s)	1.09 (3H, s)
13	1.86 (3H, d, 1)	2.04 (3H, d, 1)	2.04 (3H, d, 1)	1.86 (3H, d, 1)	2.04 (3H, d, 1)	2.04 (3H, d, 1)
1'	4.90 (1H, d, 8)	4.32 (1H, d, 8)		4.89 (1H, d, 8)	4.33 (1H, d, 8)	
2'	3.97 (1H, m)	3.15 (1H, dd, 9, 8)		3.99 (1H, dd, 9, 8)	3.14 (1H, dd, 9, 8)	
3'	4.19 (1H, m)	3.34 (1H, dd, 9, 9)		4.25 (1H, dd, 9, 9)	3.35 (1H, dd, 9, 9)	
4'	4.19 (1H, m)	3.27 (1H, dd, 9, 9)		4.20 (1H, dd, 9, 9)	3.27 (1H, m)	
5'	3.94 (1H, m)	3.25 (1H, m)		3.95 (1H, m)	3.26 (1H, m)	
6'	4.36 (1H, dd, 12, 5)	3.66 (1H, dd, 12, 5)		4.35 (1H, dd, 12, 5)	3.65 (1H, dd, 12, 5)	
	4.53 (1H, dd, 12, 2)	3.85 (1H, dd, 12, 2)		4.54 (1H, dd, 12, 2)	3.85 (1H, dd, 12, 2)	

J in Hz. m: multiplet or overlapped. Chemical shift were determined by HH-COSY and HMQC.

chemical shift of C-8 is usually affected too large by the structure and substitution pattern around six-membered ring moiety. C-9 is also affected in a similar way but slightly. The ^{13}C chemical shifts of C-9, C-10 and Glc-1 are valuable to distinguish the stereochemistry of C-9 in methanol- d_4 (Figs. 3B, D). Especially, C-10 may be the most reliable to this purpose because it locates far from other substituent. The stereochemistry of C-6 may not affect the above empirical rule by judging from the data of C-6 epimeric counterparts (Figs. 3A, C).

Several compounds published by ourselves should be revised here as follows: salvionoside C¹²) and leaoside¹³) must have 9*R* configuration, and euodionosides F and G¹⁴) are of 9*S* configuration. Lauroside E¹⁵) that was quoted as a known compound in our previous work^{16,17}) should be corrected to

have 9*R* configuration.

Experimental

General Experimental Procedures The spectral data was taken by similar procedures described previously.¹⁸) The absolute configuration of glucose was determined by HPLC analysis [JASCO OR-2090 plus: Optical rotation detector, SHODEX Asahipak NH2P-50: $\Phi=4.5$ mm, $L=25$ cm, 75% CH_3CN aq., 1 ml/min].

Blumenol C Glucoside (**1**): Amorphous powder; $[\alpha]_D^{23} +49.0^\circ$ ($c=2.15$, MeOH); IR ν_{max} (film) cm^{-1} : 3399, 2963, 1650, 1377, 1258, 1161, 1076, 1035; UV λ_{max} (MeOH) nm (log ϵ): 238 (4.06) ($c=2.30 \times 10^{-5}$ M, MeOH); ^{13}C - and ^1H -NMR ($\text{C}_5\text{D}_5\text{N}$ and CD_3OD): Tables 1 and 2; CD $\Delta\epsilon$ (nm): +0.63 (331), +4.25 (234) ($c=2.30 \times 10^{-5}$ M, MeOH); HR-ESI-TOF-MS (positive-ion mode) m/z : 395.2043 $[\text{M}+\text{Na}]^+$ (Calcd for $\text{C}_{19}\text{H}_{32}\text{O}_7\text{Na}$: 395.2040).

Byzantionoside B (**2**): Amorphous powder; $[\alpha]_D^{24} +27.0^\circ$ ($c=0.21$, MeOH); IR ν_{max} (film) cm^{-1} : 3399, 2964, 1645, 1377, 1255, 1160, 1076, 1036; UV λ_{max} (MeOH) nm (log ϵ): 239 (4.24) ($c=2.82 \times 10^{-5}$ M, MeOH);

A		C-8	C-9	C-10	Glc-1	Method
		40.6	76.6	20.0	102.3	M ⁽¹⁹⁾
		40.6	76.4	20.0	102.3	M ⁽¹⁹⁾
		39.8	76.5	19.7	102.6	M ⁽¹⁶⁾
		40.7	76.2	19.7	102.7	G ⁽²⁰⁾
		40.5	75.9	19.8	102.2	G ⁽²¹⁾
		40.7	76.1	19.7	102.2	M ⁽²¹⁾
		40.7	76.4	20.0	102.3	G ⁽²²⁾
		37.8	75.2	20.0	102.1	M ⁽²³⁾
		39.0	76.2	19.8	102.2	G ⁽²⁴⁾
		39.0	76.3	19.9	102.3	M ⁽²⁵⁾
		38.9	76.4	19.9	102.4	M ⁽²⁵⁾
		39.0	76.1	19.8	102.2	S ⁽²⁶⁾
		39.0	76.3	19.8	102.3	G ⁽²⁰⁾
		38.9	76.4	19.9	102.4	S ⁽²⁷⁾
		37.8	76.0	20.1	102.4	M ⁽¹⁸⁾
		37.6	76.7	20.4	102.9	M ^(17,18)
		34.3	76.8	20.0	102.2	G ⁽²⁸⁾
		38.8*	76.1*	19.8*	102.0*	S ⁽²⁷⁾
		38.9*	76.2*	19.9*	102.1*	S ⁽²⁷⁾
		38.0	77.9	21.8	103.9	G ⁽¹¹⁾
		38.8	77.9	21.8	103.9	S ⁽²⁶⁾
		37.9	77.9	21.8	103.9	G ⁽²⁴⁾
		34.4	77.8	21.8	103.8	M ^(29,30)
		38.0*	78.0*	21.8*	103.7*	S ⁽²⁷⁾
		38.1*	78.1*	21.9*	103.8*	S ⁽²⁷⁾
*: epimeric mixture at C-6						
(Methanol-d ₄) (Mosher's method, (G)lucosylation shift, (S)ynthesis						

B		C-9	C-10	Glc-1
	9R:	75.7~76.8	19.7~20.4	102.0~102.9
	9S:	77.7~78.1	21.8~22.0	103.7~103.9

C		C-8	C-9	C-10	Glc-1	Method
		136.4	78.0	21.6	102.2	M ⁽¹⁹⁾
		136.4	78.2	21.6	102.4	M ⁽¹⁹⁾
		138.5	77.9	21.3	102.5	M ⁽¹⁶⁾
		140.0	77.3	21.2	102.6	M ⁽³¹⁾
		141.0	78.0	21.5	103.0	M ⁽¹⁸⁾
		134.3	79.1	21.5	102.6	M ⁽¹⁶⁾
		133.6	79.1	21.8	102.9	M ⁽¹⁶⁾
		133.7	78.0	21.5	102.5	D ⁽²⁸⁾
		133.7	78.0	21.5	102.5	D ⁽²⁸⁾
		133.3	78.0	21.7	102.9	D ⁽³²⁾
		140.0	75.2	22.3	101.6	M ⁽¹¹⁾
		137.5	75.6	22.4	101.7	M ⁽¹¹⁾
		136.9	74.8	22.5	101.4	M ⁽¹⁴⁾
		136.2	74.7	22.4	101.4	M ⁽¹¹⁾
		136.1	74.8	22.5	101.4	M ⁽¹¹⁾
		133.3	75.7	22.6	100.7	M ⁽¹⁴⁾
		132.7	75.7	22.5	100.5	M ⁽¹⁴⁾
		137.0	75.6	22.6	100.9	M ⁽¹¹⁾
		133.1	75.5	22.4	100.8	M ⁽³³⁾
		137.1	76.3	22.6	101.1	M ⁽¹¹⁾
*: epimeric mixture at C-6						
(Methanol-d ₄) (Mosher's method, (D)erivatization						

D		C-9	C-10	Glc-1
	9R:	77.3~79.1	21.2~21.8	102.2~103.0
	9S:	74.7~76.3	22.3~22.6	100.5~101.7

Fig. 3. ¹³C Chemical Shifts Nature for Related Compounds

(A, C) Structures and chemical shifts, (B) chemical shift feature for 9-hydroxymegastigman 9-*O*-β-D-glucopyranosides possessing saturated C-7 to 10, (D) chemical shift feature for Δ^{7,8}-type of 9-hydroxymegastigman 9-*O*-β-D-glucopyranosides.

¹³C- and ¹H-NMR (C₅D₅N and CD₃OD): Tables 1 and 2; CD Δε (nm): +0.68 (332), +2.53 (235) (*c* = 2.82 × 10⁻⁵ M, MeOH); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 395.2038 [M+Na]⁺ (Calcd for C₁₉H₃₂O₇Na: 395.2040).

Enzymatic Hydrolysis Blumenol C glucoside (**1**) and byzantionoside B (**2**) were hydrolyzed with β-glucosidase. The aglycone and glucose was separated by TLC (CHCl₃:MeOH:H₂O, 15:6:1, *R_f* values, **1**: 0.63, aglycone (**1a**): 0.81, **2**: 0.67, aglycone (**2a**): 0.87, and glucose: 0.15). The absolute configuration of glucose was determined to be D-series by HPLC analysis. (6*R*,9*S*)-9-hydroxymegastigman-4-en-3-one, 9-*epi*-blumenol C (**1a**): gummy syrup; [α]_D²⁴ +80.5° (*c* = 0.32, CHCl₃); IR ν_{max} (film) cm⁻¹: 3416, 2964, 1658, 1374, 1255, 1126; UV λ_{max} (MeOH) nm (log ε): 239 (4.14); ¹³C- and ¹H-NMR (CD₃OD): Tables 1 and 2; CD Δε (nm): +1.65 (333), +2.54 (242) (*c* = 2.14 × 10⁻⁵ M, MeOH); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 233.1510 [M+Na]⁺ (Calcd for C₁₃H₂₂O₂Na: 233.1512). (6*R*,9*R*)-9-hydroxymegastigman-4-en-3-one, blumenol C (**2a**): gummy syrup; [α]_D²³ +46.3° (*c* = 0.08, CHCl₃); IR ν_{max} (film) cm⁻¹: 3423, 2963, 1658, 1372, 1292, 1256, 1126; UV λ_{max} (MeOH) nm (log ε): 239 (3.83) (*c* = 3.16 × 10⁻⁵ M, MeOH); ¹³C- and ¹H-NMR (CD₃OD): Tables 1 and 2; CD Δε (nm): +0.61 (327), +2.75 (231) (*c* = 2.14 × 10⁻⁵ M, MeOH); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 233.1509 [M+Na]⁺ (Calcd for C₁₃H₂₂O₂Na: 233.1512).

Preparation of (R)- and (S)-MTPA Esters MTPA esters were prepared from **1a** and **2a** by the procedure described previously.⁽¹⁸⁾ (6*R*,9*S*)-9-hydroxymegastigman-4-en-3-one (R)-MTPA ester (**1b**): Amorphous powder; ¹H-NMR (CDCl₃, 600 MHz) δ_H: 7.54—7.51 (2H, m, aromatic protons), 7.41—7.37 (3H, m, aromatic protons), 5.78 (1H, s, H-4), 5.12 (1H, m, H-9), 3.57 (3H, brs, OMe), 2.24 (1H, d, *J* = 17 Hz, H-2a), 2.00 (1H, d, *J* = 17 Hz, H-2b), 1.85 (3H, d, *J* = 1 Hz, H₃-13), 1.77 (1H, brt, *J* = 5 Hz, H-6), 1.73—1.62 (2H,

m, H₂-8), 1.58 (1H, m, H-7a), 1.34 (1H, m, H-7b), 1.36 (3H, d, *J* = 6 Hz, H₃-10), 0.98 (3H, s, H₃-11), 0.95 (3H, s, H₃-12); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 449.1907 [M+Na]⁺ (Calcd for C₂₃H₂₉O₄F₃Na: 449.1910). (6*R*,9*S*)-9-hydroxymegastigman-4-en-3-one (S)-MTPA ester (**1c**): Amorphous powder; ¹H-NMR (CDCl₃, 600 MHz) δ_H: 7.53—7.51 (2H, m, aromatic protons), 7.42—7.38 (3H, m, aromatic protons), 5.83 (1H, s, H-4), 5.10 (1H, m, H-9), 3.51 (3H, brs, OMe), 2.29 (1H, d, *J* = 17 Hz, H-2a), 2.04 (1H, d, *J* = 17 Hz, H-2b), 1.93 (3H, d, *J* = 1 Hz, H₃-13), 1.85 (1H, brt, *J* = 5 Hz, H-6), 1.78—1.68 (2H, m, H₂-8), 1.71 (1H, m, H-7a), 1.50 (1H, m, H-7b), 1.29 (3H, d, *J* = 6 Hz, H₃-10), 1.01 (6H, s, H₃-11, H₃-12); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 449.1914 [M+Na]⁺ (Calcd for C₂₃H₂₉O₄F₃Na: 449.1910). (6*R*,9*R*)-9-hydroxymegastigman-4-en-3-one (R)-MTPA ester (**2b**): Amorphous powder; ¹H-NMR (CDCl₃, 600 MHz) δ_H: 7.54—7.51 (2H, m, aromatic protons), 7.43—7.38 (3H, m, aromatic protons), 5.83 (1H, s, H-4), 5.09 (1H, m, H-9), 3.51 (3H, brs, OMe), 2.27 (1H, d, *J* = 17 Hz, H-2a), 2.02 (1H, d, *J* = 17 Hz, H-2b), 1.94 (3H, d, *J* = 1 Hz, H₃-13), 1.77 (2H, m, H₂-8), 1.77—1.68 (1H, m, H-6), 1.68 (1H, m, H-7a), 1.41 (1H, m, H-7b), 1.30 (3H, d, *J* = 6 Hz, H₃-10), 1.01 (3H, s, H₃-12), 1.00 (3H, s, H₃-11); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 449.1904 [M+Na]⁺ (Calcd for C₂₃H₂₉O₄F₃Na: 449.1910). (6*R*,9*R*)-9-hydroxymegastigman-4-en-3-one (S)-MTPA ester (**2c**): Amorphous powder; ¹H-NMR (CDCl₃, 600 MHz) δ_H: 7.56—7.51 (2H, m, aromatic protons), 7.43—7.38 (3H, m, aromatic protons), 5.80 (1H, s, H-4), 5.10 (1H, m, H-9), 3.58 (3H, brs, OMe), 2.18 (1H, d, *J* = 17 Hz, H-2a), 1.96 (1H, d, *J* = 17 Hz, H-2b), 1.87 (3H, d, *J* = 1 Hz, H₃-13), 1.72 (2H, m, H₂-8), 1.72—1.61 (1H, m, H-6), 1.61 (1H, m, H-7a), 1.30 (1H, m, H-7b), 1.36 (3H, d, *J* = 6 Hz, H₃-10), 0.92 (3H, s, H₃-11), 0.97 (3H, s, H₃-12); HR-ESI-TOF-MS (positive-ion mode) *m/z*: 449.1905 [M+Na]⁺ (Calcd for C₂₃H₂₉O₄F₃Na: 449.1910).

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