FULL PAPER

Three New Atisane Diterpenoids from *Spiraea japonica*

by **Xiang-Dong Qin**[a]), **Shu Yang**[a]), **Yan Zhao***[a]), **Li-Xia Wang**[b]), **Fu-Cai Ren**[b]), and **Fei Wang***[b])

[a]) College of Basic Science and Information Engineering, Yunnan Agricultural University, Kunming 650201, P. R. China (phone: +86 871 65226191; e-mail: zhaoyankm@126.com)

[b]) *BioBioPha Co., Ltd*., Kunming 650201, P. R. China (phone: +86 871 65215193; fax: +86 871 65215563; e-mail: wangfei@mail.kib.ac.cn)

Three new atisane diterpenoids, spiratisanins A – C (**1** – **3**, resp.), featuring a phenylacryloxyl substituted *ent*-atisane skeleton, were isolated from *Spiraea japonica* together with two known atisine diterpene alkaloids, spiramine A (**4**) and spiradine F (**5**). The structures of these new compounds were elucidated as (5*β*,7*α*,8*α*,9*β*,10*α*,12*α*,16*β*)-16-hydroxyatisan-7-yl (2*E*)-3-phenylprop-2-enoate (**1**), (5*β*,7*α*,8*α*,9*β*,10*α*,12*α*,16*α*)-16-hydroxyatisan-7-yl (2*E*)-3-phenylprop-2-enoate (**2**), and (5*β*,8*α*,9*β*,10*α*,12*α*,16*β*)-16-hydroxyatisan-20-yl (2*E*)-3-phenylprop-2-enoate (**3**) on the basis of spectroscopic analysis.

Keywords: *Spiraea japonica*, Spiratisanins A – C, Bioactivity.

Introduction

Spiraea japonica var. *acuta*, wide spread across East Asia, have been used as diuretic, detoxicant, and analgesic agents, as well as for the treatment of inflammation, cough, headache, and toothache in traditional Chinese medicine [1]. Previous phytochemical investigations of this plant have led to the discovery of two main types of compound, diterpenoids [2 – 4] and diterpene alkaloids [5 – 7], some of which have been proved to exhibit variety of bioactivities, including anti-inflammation, antiplatelet aggregation, neuroprotective [2], anti-HIV [8], and insecticidal activities [9].

As one part of our search for bioactive metabolites from the natural sources in Yunnan Province [10][11], three new atisane diterpenoids, spiratisanins A – C (**1** – **3**, respectively) (*Fig. 1*), were isolated along with two known atisine diterpenoid alkaloids, spiramine A (**4**), and spiradine F (**5**), from *S. japonica*. Spiratisanins A – C (**1** – **3**) are firstly obtained from nature with an *ent*-atisane skeleton substituted with a phenylacryloxy.

Results and Discussion

Spiratisanin A (**1**) was isolated as white powder. Its molecular formula was determined as $C_{29}H_{40}O_3$ by HR-ESI-MS (*m*/*z* 459.2874 ([*M* + Na]$^+$)), as well as its ^{1}H- and ^{13}C-NMR data. The IR spectrum indicated the presence of OH (3440 cm^{-1}), C=O (1708 cm^{-1}), and Ph (1637 and 1450 cm^{-1}) moieties. The UV spectrum showed a maximum absorption at 277 nm. The ^{1}H-NMR spectrum (*Table*) revealed the presence of four Me groups (*δ*(H) 1.29, 0.88, 0.83, and 1.02 (*s*, each 3 H)), a monosubstituted aromatic ring (*δ*(H) 7.51 – 7.53 (*m*, 2 H), 7.37 – 7.39 (*m*, 2 H), and 7.37 – 7.38 (*m*, 1 H)), and a pair of (*E*)-olefinic H-atoms (*δ*(H) 7.66 and 6.42 (*d*, *J* = 16.1, each 1 H)). The ^{13}C-NMR and DEPT spectra (*Table*) showed 29 resonances for one carboxylic ester group (*δ*(C) 166.7), one aromatic quaternary C-atom (*δ*(C) 134.5), five aromatic CH groups (*δ*(C) 128.1, 128.8, 130.1, 128.8, and 128.1), two olefinic CH groups (*δ*(C) 144.5 and 118.7), four aliphatic quaternary C-atoms (*δ*(C) 33.1, 38.6, 37.6, and 72.0), four aliphatic CH groups (*δ*(C) 53.3, 80.2, 50.7, and 37.6), eight aliphatic CH_2 groups (*δ*(C) 39.1, 18.1, 41.8, 24.3, 25.1, 21.0, 21.2, and 53.1), and four Me groups (*δ*(C) 30.7, 33.3, 21.7, and 14.0). Both HSQC and HMBC experiments yielded sufficient data to define the molecular connectivity. In the HMBC spectrum (*Fig. 2*), the correlations of H–C(7′) (*δ*(H) 7.66) with C(9′) (*δ*(C) 166.7), C(8′) (*δ*(C) 118.7), C(1′) (*δ*(C) 134.5), and C(2′/6′) (*δ*(C) 128.1), H–C(8′) (*δ*(H) 6.42) with C(7′) (*δ*(C) 144.5), C(9′) and C(1′), H–C(4′) (*δ*(H) 7.37 – 7.38) with C(2′/6′), and C(3′/5′) (*δ*(C) 128.8) suggested the existence of a phenylacryloxy fragment (**c**) (*Fig. 2*). Considering the ten degrees of unsaturation of **1**, the remaining 20 carbons were assigned to a tetracyclic diterpene moiety. The ^{1}H,^{13}C-NMR long-range correlations of Me(20) (*δ*(H) 1.02) with C(1) (*δ*(C) 39.1), C(5) (*δ*(C) 53.3), and C(10) (*δ*(C) 37.6), Me(18) (*δ*(H) 0.88), and Me(19) (*δ*(H) 0.83) with C(3) (*δ*(C) 41.8), C(4) (*δ*(C) 33.1), and C(5), H–C(5) (*δ*(H) 0.98) with C(3) and C(10), H–C(3) (*δ*(H) 1.38 – 1.44, 1.12 – 1.19) with C(1) and C(2) (*δ*(C) 18.1), and H–C(2) (*δ*(H) 1.38 – 1.43, 1.56 – 1.60) with C(10) established the fragment **a** (*Fig. 2*). Correlations of H–C(7)

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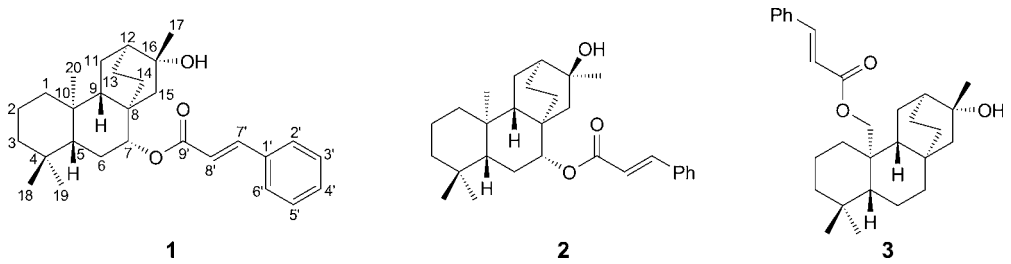

1 **2** **3**

Fig. 1. Structures of spiratisanins A – C (**1** – **3**, resp.)

Table. ^{1}H- and ^{13}C-NMR data (600 and 150 MHz, resp.) of **1** ($CDCl_3$), **2** ($CDCl_3$), and **3** (D_6)DMSO. δ in ppm, J in Hz

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	1.51 – 1.57 (*m*, H_α) 0.75 – 0.82 (*m*, H_β)	39.1	1.56 – 1.63 (*m*, H_α) 0.81 – 0.89 (*m*, H_β)	38.8	2.03 – 2.09 (*m*, H_α) 0.76 – 0.83 (*m*, H_β)	34.8
2	1.38 – 1.43 (*m*, H_α) 1.56 – 1.60 (*m*, H_β)	18.1	1.41 – 1.46 (*m*, H_α) 1.56 – 1.66 (*m*, H_β)	18.0	1.36 – 1.42 (*m*, H_α) 1.54 – 1.60 (*m*, H_β)	19.1
3	1.38 – 1.44 (*m*, H_α) 1.12 – 1.19 (*m*, H_β)	41.8	1.40 – 1.46 (*m*, H_α) 1.15 – 1.23 (*m*, H_β)	41.8	1.37 – 1.42 (*m*, H_α) 1.13 – 1.20 (*m*, H_β)	41.4
4		33.1		33.0		32.7
5	0.98 (*dd*, *J* = 12.5, 1.8)	53.3	1.03 (*dd*, *J* = 12.3, 1.4)	53.1	0.91 (br. *d*, *J* = 12.6)	55.7
6	1.48 – 1.53 (*m*, H_α) 1.74 – 1.80 (*m*, H_β)	24.3	1.46 – 1.54 (*m*, H_α) 1.78 – 1.84 (*m*, H_β)	24.5	1.21 – 1.27 (*m*, H_α) 1.41 – 1.45 (*m*, H_β)	18.0
7	4.68 (*dd*, *J* = 11.7, 4.8)	80.2	4.75 (*dd*, *J* = 11.6, 4.8)	80.4	1.34 – 1.40 (*m*, H_α) 1.03 – 1.10 (*m*, H_β)	39.6
8		38.6		38.5		33.2
9	1.07 (*dd*, *J* = 11.6, 6.6)	50.7	1.34 (*dd*, *J* = 11.2, 6.7)	50.3	1.06 – 1.12 (*m*)	51.0
10		37.6		37.7		40.5
11	1.33 – 1.39 (*m*, H_α) 1.63 – 1.70 (*m*, H_β)	25.1	1.20 – 1.26 (*m*, H_α) 2.04 – 2.11 (*m*, H_β)	23.0	1.59 – 1.62 (*m*)	25.1
12	1.53 – 1.58 (*m*)	37.6	1.57 – 1.61 (*m*)	37.6	1.37 – 1.41 (*m*)	37.1
13	1.55 – 1.61 (*m*, H_a) 1.74 – 1.80 (*m*, H_b)	21.0	1.50 – 1.57 (*m*, H_a) 1.67 – 1.74 (*m*, H_b)	23.0	1.17 – 1.23 (*m*, H_a) 1.98 – 2.05 (*m*, H_b)	21.8
14	2.06 – 2.12 (*m*, H_a) 1.34 – 1.40 (*m*, H_b)	21.2	1.74 – 1.82 (*m*, H_a) 1.33 – 1.41 (*m*, H_b)	20.8	1.68 – 1.74 (*m*, H_a) 1.01 – 1.08 (*m*, H_b)	27.5
15	1.66 (*d*, *J* = 13.5, H_α) 1.24 (*d*, *J* = 13.5, H_β)	53.1	1.68 (*d*, *J* = 13.7, H_α) 1.25 (*d*, *J* = 13.7, H_β)	53.0	1.26 (*d*, *J* = 13.0, H_α) 1.08 (*d*, *J* = 13.0, H_β)	57.9
16		72.0		71.5		69.9
17	1.29 (*s*)	30.7	1.30 (*s*)	30.5	1.15 (*s*)	30.7
18	0.88 (*s*)	33.3	0.91 (*s*)	33.3	0.87 (*s*)	33.5
19	0.83 (*s*)	21.7	0.85 (*s*)	21.7	0.87 (*s*)	21.1
20	1.02 (*s*)	14.0	1.03 (*s*)	14.0	4.52 (*d*, *J* = 12.6) 4.49 (*d*, *J* = 12.6)	63.1
1′		134.5		134.5		133.9
2′	7.51 – 7.53 (*m*)	128.1	7.55 – 7.59 (*m*)	128.0	7.72 – 7.75 (*m*)	128.5
3′	7.37 – 7.39 (*m*)	128.8	7.39 – 7.44 (*m*)	128.9	7.41 – 7.45 (*m*)	129.0
4′	7.37 – 7.38 (*m*)	130.1	7.39 – 7.43 (*m*)	130.2	7.43 – 7.44 (*m*)	130.6
5′	7.37 – 7.39 (*m*)	128.8	7.39 – 7.44 (*m*)	128.9	7.41 – 7.45 (*m*)	129.0
6′	7.51 – 7.53 (*m*)	128.1	7.55 – 7.59 (*m*)	128.0	7.72 – 7.75 (*m*)	128.5
7′	7.66 (*d*, *J* = 16.1)	144.5	7.69 (*d*, *J* = 16.0)	144.4	7.64 (*d*, *J* = 16.0)	144.6
8′	6.42 (*d*, *J* = 16.1)	118.7	6.46 (*d*, *J* = 16.0)	118.6	6.66 (*d*, *J* = 16.0)	118.2
9′		166.7		166.6		166.4
16-OH					4.09 (*s*)	

(δ(H) 4.68) with C(6) (δ(C) 24.3), C(8) (δ(C) 38.6), C(14) (δ(C) 21.2), and C(15) (δ(C) 53.1), H–C(9) (δ(H) 1.07) with C(11) (δ(C) 25.1), C(12) (δ(C) 37.6), C(14), and C(15), H–C(12) (δ(H) 1.53 – 1.58) with C(13) (δ(C) 21.0) and C(14), Me(17) (δ(H) 1.29) with C(15) and C(16) (δ(C) 72.0) afforded the fragment **b** (*Fig. 2*). All of the three sub-

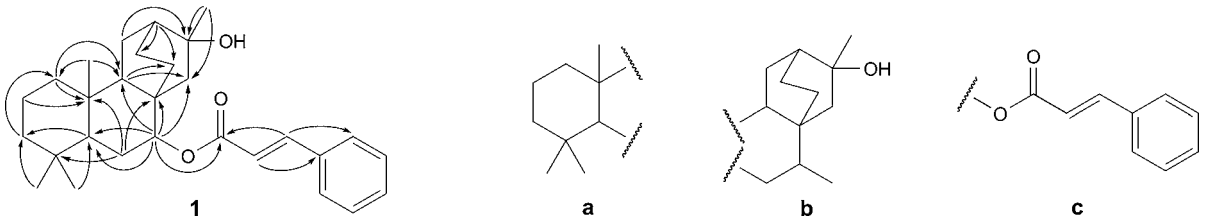

Fig. 2. Selected HMBCs (H→C) and substructures of **1**

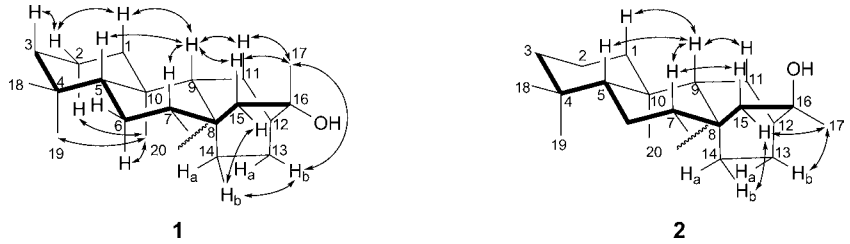

Fig. 3. Selected ROESY (H↔H) correlations of **1** and **2**

structures were connected by the HMBC correlations of H–C(7) with C(5) and C(9′), and H–C(9) with C(20) (δ(C) 14.0). Thus, compound **1** was established to be a phenylacryloxy-substituted *ent*-atisane diterpene.

The relative configuration of **1** was determined on the basis of ROESY correlations (*Fig. 3*). As a reference point, the β orientation of H–C(9) and H–C(5) and α orientation of Me(20) were used, which are characteristic for atisane diterpene. The ROESY correlations of H–C (9) with H–C(7), H_β–C(11) (δ(H) 1.63 – 1.70) and H_β–C (15) (δ(H) 1.24), and of Me(17) with H_β–C(11) and H_β–C (15) indicated β-configuration for both H–C(7) and Me (17) group. As a result, **1** was elucidated as (5β,7α,8α,9β,10α,12α,16β)-16-hydroxyatisan-7-yl (2*E*)-3-phenylprop-2-enoate.

Spiratisanin B (**2**) was isolated as white powder. Its molecular formula was established as $C_{29}H_{40}O_3$ by HR-ESI-MS (*m*/*z* 459.2870 ([*M* + Na]$^+$)), as well as its ^{1}H- and ^{13}C-NMR data. The IR spectrum showed the presence of OH (3442 cm^{-1}), C=O (1707 cm^{-1}), and Ph (1638 and 1450 cm^{-1}) moieties. The UV spectrum showed a maximum absorption at 277 nm. The ^{13}C-NMR and DEPT spectra (*Table*) showed 29 resonances for one carboxylic ester group (δ(C) 166.6), one aromatic quaternary C-atom (δ(C) 134.5), five aromatic CH groups (δ(C) 128.0, 128.9, 130.2, 128.9, and 128.0), two olefinic CH groups (δ(C) 144.4 and 118.6), four aliphatic quaternary C-atoms (δ(C) 33.0, 38.5, 37.7, and 71.5), four aliphatic CH groups (δ(C) 53.1, 80.4, 50.3, and 37.6), eight aliphatic CH_2 groups (δ(C) 38.8, 18.0, 41.8, 24.5, 23.0, 23.0, 20.8, and 53.0), and four Me groups (δ(C) 30.5, 33.3, 21.7, and 14.0). The comparative study of the NMR, IR, and UV spectra of **2** and **1** indicated that the two compounds are very similar. The principal differences in the ^{13}C-NMR spectra appeared at the signals of C(11) (δ(C) 25.1 in **1** and 23.0 in **2**) and C(13) (δ(C) 21.0 in **1** and 23.0 in **2**). The HMBC spectra of **2** established the same carbon connections with **1**. Considering the obviously different optical rotations of the two compounds, **2** was determined to be an optical isomer of **1**. The conclusion was also supported by ROESY analysis. In the ROESY spectrum (*Fig. 3*), correlations of H–C(9) (δ(H) 1.34) with H–C(7) (δ(H) 4.75) and H_β–C(15) (δ(H) 1.25), and of Me(17) (δ(H) 1.30) with H_α–C(15) (δ(H) 1.68) and H_b–C(13) (δ(H) 1.67 – 1.74) could be observed, indicating the β-position of H–C(7) and the α-position of Me(17). Thus, **2** was identified as (5β,7α,8α,9β,10α,12α,16α)-16-hydroxyatisan-7-yl (2*E*)-3-phenylprop-2-enoate.

Spiratisanin C (**3**) was isolated as white powder. Its molecular formula was established as $C_{29}H_{40}O_3$ by HR-ESI-MS (*m*/*z* 459.2872 ([*M* + Na]$^+$)), as well as its ^{1}H- and ^{13}C-NMR data. The IR spectrum showed the presence of OH (3439 cm^{-1}), C=O (1709 cm^{-1}), and Ph (1637 and 1449 cm^{-1}) moieties. The UV spectrum showed a maximum absorption at 277 nm. The ^{13}C-NMR and DEPT spectra (*Table*) showed 29 resonances for one carboxylic ester group (δ(C) 166.4), one aromatic quaternary C-atom (δ(C) 133.9), five aromatic CH groups (δ(C) 128.5, 129.0, 130.6, 129.0, and 128.5), two olefinic CH groups (δ(C) 144.6 and 118.2), four aliphatic quaternary C-atoms (δ(C) 32.7, 33.2, 40.5, and 69.9), three aliphatic CH groups (δ(C) 55.7, 51.0, and 37.1), ten aliphatic CH_2 groups (δ(C) 34.8, 19.1, 41.4, 18.0, 39.6, 25.1, 21.8, 27.5, 57.9, and 63.1), and three Me groups (δ(C) 30.7, 33.5, and 21.1). The above data suggested that **3** was also a phenylacryloxy-substituted *ent*-atisane diterpene. The principal difference in the NMR data was that **3** exhibited two more aliphatic CH_2 signals than **1** and **2**, accompanying with the missing of one aliphatic CH signal in low field and one Me signal in high field. In the HMBC spectrum, correlations of CH_2(20) (δ(H) 4.52, 4.49) with C(9′) (δ(C) 166.4), C(1) (δ(C) 34.8), C(5) (δ(C) 55.7), C(9) (δ(C) 51.0), and C(10)

(δ(C) 40.5) could be observed, indicating the connection of phenylacryloxy group with C(20) (δ(C) 63.1). In the ROESY spectrum, the obvious correlation between HO–C(16) (δ(H) 4.09) and H_b–C(13) (δ(H) 1.98 – 2.05) suggested β-configuration for Me(17) group. Thus, **3** was identified as (5β,8α,9β,10α,12α,16β)-16-hydroxyatisan-20-yl (2*E*)-3-phenylprop-2-enoate.

The known compounds were identified as spiramine A (**4**) [12] and spiradine F (**5**) [13] by comparing the spectroscopic data with those reported.

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Experimental Part

General

TLC: silica gel *GF254* (SiO_2; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China). Column chromatography (CC): SiO_2 (100 – 200 and 200 – 300 mesh; *Qingdao Marine Chemical Factory*), *Sephadex LH-20* (*Amersham Biosciences*, Uppsala, Sweden). Medium-pressure liquid chromatography (MPLC): *Büchi* fraction collector *C-660*, *Büchi* pump module *C-605*, *Büchi* pump manager *C-615*, *Büchi* column (240 × 20 mm), and *Chromatorex C-18* (40 – 75 μm, *Fuji Silysia Chemical Ltd.*, Japan). Prep. HPLC: *Agilent ZORBAX SB-C18 ODS* columns (21.2 mm × 150 mm, 5 μm). Optical rotations: *Jasco P-1020* digital polarimeter. UV Spectra: *Agilent 1200* HPLC; λ_{max} in nm. IR Spectra: *Bruker Tensor 27* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker Avance III 600* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS and HR-ESI-MS: *Agilent 6230 TOF* mass spectrometer; in *m*/*z* (rel. %).

Plant Material

Spiraea japonica was collected from Yunnan Province, China, in April, 2008, and was identified by Mr. *Yu Chen* at Kunming Institute of Botany, CAS. A voucher specimen (No. BBP0049) was deposited at *BioBioPha*.

Extraction and Isolation

The dried and powdered whole plant of *S. japonica* (6.5 kg) were extracted with 95% aq. EtOH (3 × 25 l) at room temperature for 7 days. The EtOH extract was evaporated to yield a thick, dark extract (*ca.* 250 g), which was subjected to CC (SiO_2; petroleum ether (PE)/acetone 20:1→0:1) to yield seven fractions. *Fr. 3* (60 g) was further separated by CC (SiO_2; PE/acetone 100:1→2:8) to give four fractions. *Frs. 3.2* and *3.3* were further separated by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1; SiO_2; PE/acetone 100:1) to afford **4** (57 mg) and **5** (792 mg), resp. *Fr. 4* (42 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 100:1→50:1) to give six fractions. *Fr. 4.2* was further separated by MPLC (MeOH/H_2O 85:15→95:5) to afford five fractions. *Fr. 4.2.2* was purified by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1) to afford **1** (10 mg). *Fr. 4.2.3* was separated by prep. HPLC (MeOH/H_2O 9:1) to yield **2** (15 mg) and **3** (14 mg).

Spiratisanin A (= (5β,7α,8α,9β,10α,12α,16β)-16-Hydroxyatisan-7-yl (2*E*)-3-Phenylprop-2-enoate; **1**). White powder. $[\alpha]_D^{23.9}$ = −43.3 (*c* = 0.13, $CHCl_3$/MeOH, 2:1). UV (MeOH): 217, 222 (sh), 277. IR (KBr): 3440, 1708, 1637, 1450, 1368, 1272. ^{1}H- and ^{13}C-NMR ($CDCl_3$): *Table*. HR-ESI-MS: 459.2874 ($[M + Na]^+$, $C_{29}H_{40}NaO_3^+$; calc. 459.2875).

Spiratisanin B (= (5β,7α,8α,9β,10α,12α)-16-Hydroxyatisan-7-yl (2*E*)-3-Phenylprop-2-enoate; **2**). White powder. $[\alpha]_D^{24.1}$ = −78.3 (*c* = 0.20, MeOH). UV (MeOH): 217, 222 (sh), 277. IR (KBr): 3442, 1707, 1638, 1450, 1369, 1310. ^{1}H- and ^{13}C-NMR ($CDCl_3$): *Table*. HR-ESI-MS: 459.2870 ($[M + Na]^+$, $C_{29}H_{40}NaO_3^+$; calc. 459.2875).

Spiratisanin C (= **(5β,8α,9β,10α,12α,16β)-16-Hydroxyatisan-20-yl (2*E*)-3-Phenylprop-2-enoate**; **3**). White powder. $[\alpha]_D^{24.2}$ = −4.9 (*c* = 0.21, MeOH). UV (MeOH): 216, 221 (sh), 278. IR (KBr): 3439, 1709, 1637, 1449, 1310. ^{1}H- and ^{13}C-NMR (DMSO-d_6): *Table*. HR-ESI-MS: 459.2872 ($[M + Na]^+$, $C_{29}H_{40}NaO_3^+$; calc. 459.2875).

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