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Taxuyunnanines S-V, New Taxoids from *Taxus yunnanensis*

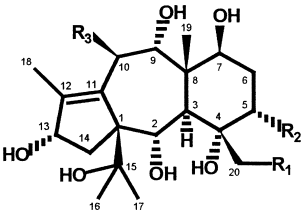
Abstract

Four new 11(15→1)-*abeo*taxoids with an opened oxetane ring system, taxuyunnanines S, T, U and V (**1 – 4**) were isolated from the bark of *Taxus yunnanensis*. Taxuyunnanine S (**1**), is the most hydroxylated *abeo*taxoid discovered to date from *Taxus* species. The structures were determined by spectroscopic means including 1D and 2D NMR experiments.

Key words
Taxus yunnanensis · Taxaceae · bark · 11(15→1)-*abeo*taxoids · taxuyunnanines S, T, U and V · 1D and 2D NMR

Introduction

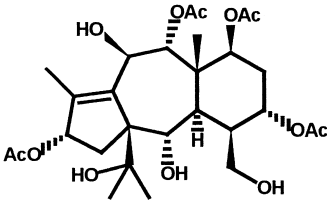
Taxus yunnanensis, Cheng, et L. K. Fu (Taxaceae) is mainly distributed in Yunnan Province, the Peoples Republic of China. It has been shown to be a rich resource of paclitaxel and related taxanes [1], [2], with more than 80 new taxoids, including every known taxane sub-type, discovered from this plant. Our previous studies on roots and bark of *T. yunnanensis* have yielded several different types of new taxanes [3 – 9]. Our continuing study on the ethanol extract of bark has led to the isolation of four additional new taxane diterpenoids having an opened oxetane ring system. We report herein the isolation and structure elucidation of taxuyunnanines S-V (**1 – 4**).



1 R_1=R_2=R_3=OH

2 R_1=R_2=OAc, R_3=OH

3 R_1=R_2=OAc, R_3=OBz



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Materials and Methods

General

1D and 2D NMR experiments were performed either on a Bruker AM-400 or DRX-500 spectrometer. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. FABMS and HRFABMS were taken on a VG Auto Spec-3000 or a Finnigan MAT 90 instrument. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectral data were obtained on a UV 210A spectrometer. Optical rotations were carried out on a HORIBA SEPA-300 High Sensitive Polarimeter or Perkin-Elmer model 241 Polarimeter. Column chromatogrphy was performed either on silica gel (200 – 300 mesh, Qingdao Marine Chemical Inc., China), silica gel H (10 – 40 μ, Qingdao Marine Chemical Inc., China), Lichroprep Rp_{18} gel (40 – 63 μm, Merck, Darmstadt, Germany), or on MCI gel (70 –

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150 μ, Mitsubishi Chemical Corporation, Tokyo, Japan). Fractions were monitored by TLC on silica gel and spots were visualized by heating plates sprayed with 10% H_2SO_4 in EtOH.

Plant material

The bark of *Taxus yunnanensis*, Cheng et L. K. Fu (Taxaceae) was collected in Lijiang Prefecture of Yunnan Province of Peoples Republic of China. A voucher specimen (No. YAF-97 – 18) has been deposited at the Yunnan Academy of Forestry, Kunming, Yunnan, People's Republic of China.

Extraction and isolation

Dried bark (50 kg) was milled, extracted and fractionated by silica gel column chromatography by gradient elution with $CHCl_3$ by increasing the concentration of Me_2CO [$CHCl_3$-Me_2CO/10 : 0 (25.0 l), 9 : 1 (30.5 l), 8 : 2 (23.5 l), 7 : 3 (16.5 l), 0 : 10 (13.5 l), respectively] as described previously [8], [9]. The $CHCl_3$-Me_2CO/7 : 3 eluate (7.2 g) was rechromatographed on silica gel (150 g, 200 – 300 mesh), eluting with $CHCl_3$-*i*-PrOH (9 : 1) to afford 12 fractions (200 ml each), of which fraction 7 was chromatographed over RP_{18} silica gel (100 g), eluting with MeOH-H_2O (2 : 1) (600 ml) to yield compound **4** (71 mg). The Me_2CO (100%) eluate was filtered and evaporated to afford 38 g of a residue, which was subjected to further silica gel (500 g, 200 – 300 mesh) cc, using $CHCl_3$-MeOH as eluent in ascending order of polarity to give 70 fractions (500 ml each). Fractions 8 – 13 were combined (2.2 g) and chromatographed on MCI gel (50 g), eluting with MeOH-H_2O (3 : 7, 500 ml) to give 10 fractions (50 ml each). Fractions 5 – 7 were further combined and chromatographed on RP_{18} silica gel (30 g) eluting with acetonitrile-H_2O (2 : 8) to provide 6 fractions (50 ml each), of which fraction 4 was rechromatographed on silica gel (30 g, 10 – 40 μ) eluting with $CHCl_3$-*i*-PrOH (6 : 1, 150 ml) to furnish compounds **2** (27 mg) and **3** (20 mg). Fractions 59 – 70 were combined (3.0 g) and repeatedly decolorized on MCI gel (50 g) with MeOH-H_2O (1 : 5) to remove most of a red colored substance. The decolorized residue was chromatographed on silica gel (50 g, 10 – 40 μ) cc, eluting with a mixture of $CHCl_3$-MeOH (8 : 2) to produce 8 fractions (100 ml each). Fractions 5 – 7 were further chromatographed on RP_{18} silica gel (30 g) eluting with MeOH-H_2O (1 : 5) to supply 4 fractions (60 ml each), of which fraction 3 was subjected to preparative silica gel TLC (10 × 20 cm, 20 g, 10 – 40 μ), developing with *i*-PrOH-$CHCl_3$/2 : 1 (100 ml) to yield compound **1** (14 mg).

Taxuyunnanine S (**1**): $C_{20}H_{34}O_9$, white powder, $[\alpha]_D^{15.5}$: –4.29° (*c* 0.70, MeOH); UV: λ_{max}^{MeOH} (log ε) = 207 nm (4.11); IR (KBr): ν_{max} = 3389, 2926, 1574, 1383, 1238, 1157, 1109, 1055, 939, 898, 738, 704 cm^{-1}. Negative FABMS: *m/z* = 417 (35) $[M-H]^+$, 339 (45), 325 (56), 311 (47), 297 (34), 281 (27), 255 (100), 219 (12), 205 (17), 184 (91), 127 (6), 92 (34), 80 (16), 60 (6); HRFABMS: *m/z* = 417.2133, required: 417.2125; ^{1}H-NMR data see Table **1**; ^{13}C-NMR data see Table **2**.

Taxuyunnanine T (**2**): $C_{24}H_{38}O_{11}$, colorless amorphous solid, $[\alpha]_D^{14.2}$: +6.85° (*c* 1.35, MeOH); UV: λ_{max}^{MeOH} (log ε) = 207 nm (4.02); IR (KBr): ν_{max} = 3398, 2985, 2888, 1726, 1380, 1249, 1153, 1115, 1064, 1042, 985, 935, 865, 839, 783, 739, 609 cm^{-1}; Negative FABMS: *m/z* = 501 (100) $[M-H]^+$, 484 (19), 441 (51), 399 (4), 323 (2), 189 (7), 171 (6), 155 (7), 127 (9), 99 (100); HRFABMS: *m/z* = 501.2341, required: 501.2336; ^{1}H-NMR data see Table **1**; ^{13}C-NMR data see Table **2**.

Table **1** ^{1}H-NMR data of compounds **1 – 4** (500 MHz, 400 MHz, *J* in Hz, δ in ppm)

Proton	*1*[a, d]	*2*[a, c]	*3*[b, d, e]	*4*[a, c]
H-2	4.42 (1H, d, 7.4)	5.18 (1H, d, 8.0)	4.62 (1H, d, 7.3)	5.18 (1H, d, 9.0)
H-3	2.53 (1H, d, 7.6)	3.39 (1H, d, 7.0)	2.67 (1H, d, 7.3)	2.99 (1H, d, 4.3, 7.9)
H-4	–	–	–	2.92 (1H, m)
H-5	3.74 (1H, brt, 3.0)	5.77 (1H, brs)	5.15 (1H, brs)	5.43 (1H, brd, 1.5)
H-6a	1.86 (1H, m)	2.36 (1H, m, H_2-6)	1.92 (2H, m, H_2-6)	2.16 (1H, m)
H-6b	1.74 (1H, m)			2.07 (1H, dt, 3.8, 14.2)
H-7	4.10 (1H, dd, 4.8, 11.4)	4.66 (1H, dd, 6.2, 9.8)	4.22 (1H, t, 8.0)	5.79 (1H, dd, 5.1, 11.0)
H-9	3.96 (1H, d, 9.6)	4.77 (1H, d, 9.6)	4.46 (1H, d, 11.1)	6.34 (1H, d, 10.5)
H-10	4.43 (1H, d, 9.8)	5.15 (1H, d, 9.0)	6.33 (1H, d, 10.4)	5.14 (1H, d, 10.3)
H-13	4.47 (1H, t, 7.0)	5.03 (1H, t, 6.9)	5.22 (1H, t. 7.4)	5.91 (1H, t, 7.5)
H-14a	2.02 (1H, dd, 7.1, 14.0)	2.74 (1H, dd, 7.1, 13.9)	2.15 (1H, dd, 7.1,1 1.7)	2.60 (1H, dd, 7.1, 14.6)
H-14b	1.78 (1H, dd, 7.7, 14.1)	2.39 (1H, dd, 7.1, 13.8)	1.95 (1H, m)	2.21 (1H, dd, 7.4, 14.3)
Me-16	1.33 (3H, s)	1.75 (3H, s)	1.38 (3H, s)	1.80 (3H, s)
Me-17	1.06 (3H, s)	1.41 (3H, s)	1.23 (3H, s)	1.37 (3H, s)
Me-18	1.85 (3H, brd, 0.9)	2.20 (3H, s)	1.88 (3H, s)	2.03 (3H, s)
Me-19	1.22 (3H, s)	1.63 (3H, s)	1.28 (3H, s)	1.43 (3H, s)
H-20a	4.00 (1H, ABd, 11.5)	5.39 (1H, ABd, 11.8)	4.76 (1H, d, 12.1)	4.30 (1H, dd, 7.4, 10.3)
H-20b	3.65 (1H, ABd, 11.5)	4.80 (1H, ABd, 11.8)	5.49 (1H, d, 12.6)	3.48 (1H, dd, 8.2, 10.3)
OAc		2.31 (3H, s)	2.15 (3H, s)	2.15 (3H, s), 2.14 (3H, s)
		1.88 (3H, s)	2.10 (3H, s)	2.04 (3H, s), 2.03 (3H, s)

[a] Data were run on 500 MHz NMR spectrometer.
[b] Data were run on 400 MHz NMR spectrometer.
[c] Data were obtained in pyridine-d_5.
[d] Data were obtained in CD_3OD.
[e] Signals of 10-OBz: 8.02 (2H, d, 7.4), 7.58 (1H, t 7.2), 7.46 (2H, t, 7.5).

Table **2** ^{13}C-NMR data of compounds **1 – 4** (500 MHz, 400 MHz, δ in ppm)

Carbon	*1*[a, d]	*2*[b, c]	*3*[b, d, e]	*4*[b, c]
1	69.2 s	69.9 s	69.7 s	69.8 s
2	70.1 d	69.4 d	70.1 d	65.8 d
3	44.0 d	44.8 d	45.3 d	42.4 d
4	78.6 s	76.6 s	77.0 s	44.1 d
5	70.1 d	71.8 d	72.3 d	71.2 d
6	35.0 t	33.2 t	33.0 t	30.6 t
7	70.8 d	70.1 d	70.6 d	70.5 d
8	44.1 s	44.0 s	44.4 s	44.3 s
9	81.8 d	81.7 d	79.0 d	80.7 d
10	69.8 d	69.9 d	72.7 d	67.1 d
11	139.9 s	140.0 s	137.5 s	139.7 s
12	145.8 s	144.9 s	150.3 s	143.3 s
13	78.6 d	77.2 d	77.3 d	80.6 d
14	39.7 t	39.4 t	39.3 t	37.8 t
15	77.6 s	76.6 s	77.6 s	76.0 s
16	26.7 q	27.2 q	27.4 q	27.6 q
17	28.1 q	28.7 q	27.8 q	28.2 q
18	11.3 q	11.8 q	11.9 q	11.2 q
19	14.5 q	15.8 q	15.1 q	11.4 q
20	66.0 t	66.1 t	66.3 t	62.0 t
OAc		171.0 s, 170.9 s, 21.4 q, 20.7 q	172.9 s, 172.4 s, 21.3 q, 20.7 q	170.9 (2C, s), 170.1 s, 169.9 s, 21.7 q, 21.4 q, 21.2 (2C, q)

[a] Data were run on 500 MHz NMR spectrometer.
[b] Data were run on 400 MHz NMR spectrometer.
[c] Data were obtained in pyridine-d_5.
[d] Data were obtained in CD_3OD.
[e] Signals of 10-OBz: 167.3 s, 131.8 s, 130.8 (2C, d), 129.5 (2C, d), 134.1 d.

Taxuyunnanine U (**3**): $C_{31}H_{42}O_{12}$, white powder, $[\alpha]_D^{15.7}$: –13.77° (*c* 0.46, MeOH); UV : λ_{max}^{MeOH} (log ε) = 202 (4.20), 228 nm (4.12); IR (KBr): ν_{max} = 3412, 2983, 1723, 1448, 1378, 1266, 1176, 1114, 1068, 1041, 976, 940, 863, 780, 713, 606 cm^{-1}; Negative FABMS: *m/z* = 606 (8) $[M]^+$, 545 (2), 484 (5), 442 (2), 325 (8), 263 (2), 173 (2), 121 (100), 77 (11); HRFABMS: *m/z* = 605.2632, required: 605.2598; ^{1}H-NMR data see Table **1**; ^{13}C-NMR data see Table **2**.

Taxuyunnanine V (**4**): $C_{28}H_{42}O_{12}$, colorless amorphous solid, $[\alpha]_D^{16.2}$: –8.57° (*c* 0.35, MeOH); UV: λ_{max}^{MeOH} (log ε) = 205 nm (4.07); IR (KBr) ν_{max} = 3426, 2983, 2950, 1735, 1731, 1437, 1375, 1250, 1146, 1094, 1027, 982, 944, 782, 606 cm^{-1}; Negative FABMS: *m/z* = 569 (28) $[M-H]^+$, 509 (10), 449 (8), 433 (9), 373 (39), 59 (100); HRFABMS *m/z* = 569.2651, required: 569.2598; ^{1}H-NMR data see Table **1**; ^{13}C-NMR data see Table **2**.

Results and Discussion

The ethanol extract of bark from *T. yunnanensis* was partitioned with $CHCl_3$ and the $CHCl_3$-soluble fraction was chromatographically separated to afford compounds **1 – 4** as described in the experimental section.

Compound **1** was obtained as a white powder with a molecular formula of $C_{20}H_{34}O_9$ based on the $[M-H]^+$ ion at *m/z* 417 in the negative FABMS, which was in agreement with its HRFABMS experiment (*m/z* 417.2133, calcd: 417.2125, $[M-H]^+$). It was recognized as a taxane diterpenoid by the presence of characteristic methyl signals [δ = 1.33, 1.06, 1.85, 1.22 (each 3H, s)] and the easily distinquished H-3 doublet (δ = 2.5) in the ^{1}H-NMR spectrum (Table **1**). It was furtherly determined to be an 11(15→1)-*abeo*taxoid from the ^{13}C-NMR signals of C-1 [δ = 69.2 (s)] and C-15 [δ 77.6 (s)] (Table **2**). The δ_C of C-20 in **1** was shifted remarkably upfield to δ = 66.0 ppm in contrast to normal *abeo*taxanes possessing an oxetane ring at *ca* δ_C = 75 ppm. This upfield shift indicated the opening of the C-4(20)-oxetane ring moiety, resulting in an increase of the coupling constant for H-20a/H-20b. The nine ^{13}C-NMR signals between δ = 65 and 80 (Table **2**) showed **1** to be a highly oxygenated compound. The consideration of **1** being a polyhydroxylated taxoid is supported by its being purified from a very polar fraction by preparative TLC using $CHCl_3$-*i*-PrOH (1 : 2) as developing solvent (R_f 0.4) and that only two strong bands due to the hydroxy adsorption at 3389 cm^{-1} and 1055 cm^{-1}, but no carbonyl band were observed in the IR spectrum. Additionally, no ester signals were observed in the ^{1}H- and ^{13}C-NMR spectra, thus confirming that the oxygenated carbons in **1** contain hydroxy groups.

The relative configuration of asymmetric carbons in **1** was determined by means of a 2D ROESY experiment (Table **3**). The observation of ROEs between H-2/Me-19 and Me-17, H-20b/Me-19, H-9/Me-19, as well as H-13/Me-17 established the hydroxys at C-2, C-4, C-9 and C-13 as α oriented. The ROE correlations between H-7/H-3 and H-10/H-3 disclosed the hydroxys at C-7 and C-10 as β-oriented. The C-5 hydroxy in the ^{1}H-NMR (Table **1**) was established to be an α orientation due to its coupling pattern (δ 3.74, brt, *J* = 3.0 Hz) (10). Lastly, the unambiguous assignments of ^{1}H-

Table **3** ROESY correlations of compounds **1 – 4** (500 MHz)

Proton	*1*	*2*	*3*	*4*
H-2	H-9, Me-16, 19	Me-16, 19	Me-19	H-3, 20a, Me-16, 19
H-3	H-7, 10, 14b	H-7, 14a	H-7	H-3, 4, 7, 14b, Me-18
H-4				H-5, 14b, H_2-20
H-5	H_2-6	H_2-6	H_2-6	H-4, 6a
H-6a	H-6b, 7	H-5, 6b	H-5, 7	H-5, 7
H-6b	H-5, 6a	H-5, 6a	H-5, 7	H-5, 7
H-7	H-3, 6a, 10	H-3	H-3, H_2-6	H-3, 10, H_2-6
H-9	H-2, Me-19	Me-18, 19	Me-19	H-2, Me-19
H-10	H-3, 7, Me-18	H-3, 14a, Me-18	H-7, Me-18	H-3, 4, 7
H-13	H-14a, Me-17	H_2-14, Me-17, 18	H-14, Me-17	H-14a, Me-17, 18
H-14a	H-13, 14b, Me-16, 17	H-3, 14b	H-13, 14b	H-13, 14b
H-14b	H-14a	H-13, 14a	H-13, 14a	H-3, 4, 14a
Me-16	H-2, 14a, Me-17	H-2, Me-17	H-2, Me-17	H-2, 14a, Me-17
Me-17	H-13, 14a, Me-16	H-13, Me-16	H-2, 13, Me-16	H-13, 14a, Me-16
Me-18	H-10	H-9, 10, 13	H-10, 13	H-10, 13
Me-19	H-2, 6b, 9, 20b	H-2, 9, H_2-20	H-2, 9, H_2-20	H-2, 9, H_2-20
H-20a	H-20b	Me-19, H-20b	Me-19	H-2, 5, 20b
H-20b	Me-19, H-20a	Me-19, H-20a	Me-19	H-5, 20a

and ^{13}C-NMR data of **1** were obtained by using 2D NMR (including ^{1}H-^{1}H COSY, HMQC and HMBC) techniques. Therefore, taxuyunnanine S (**1**) was determined to be 2α,4α,5α,7β,9α,10β,13α,15,20-nonahydroxy-11(15→1)*abeo*taxa-11-ene.

Compound **2**, a colorless amorphous solid, has a molecular formula of $C_{24}H_{38}O_{11}$ as shown by its HRFABMS (*m/z* 501.2341, calcd: 501.2336). The similarity of its NMR spectra to those of **1** established it to be another *abeo*taxoid with an opened oxetane ring. Unlike compound **1**, **2** has two esters, which were defined as acetyl groups according to the ^{1}H- and ^{13}C-NMR data. One of the acetoxys was positioned at C-20 due to the presence of cross-peaks between H_2 – 20 and an OAc-C = O in the HMBC spectrum. Meanwhile, the HMBC correlation (Tab. **4**) between H-5 and the rest acetyl carbonyl carbon allowed assignment of the second acetoxy group at C-5. Since **2** showed an equivalent coupling pattern with that of **1**, it follows that it has the same relative stereochemistry as **1**, which was further confirmed by the ROESY experiment (Tab. **3**). Compound **2** was thus established as the 2α,4α,7β,9α,10β,13α,15-heptahydroxy-5α,20-diacetoxy-11(15→1)-*abeo*taxa-11-ene, and given the trivial name taxuyunnanine T.

Compound **3**, a white powder, was shown to have a molecular formula of $C_{31}H_{42}O_{12}$ by HRFABMS (found: *m/z* 605.2632, calcd: 605.2598). A comparison of ^{1}H- and ^{13}C-NMR spectra between **3** and **2** showed that the two compounds are closely related. Besides two acetoxys at C-20 and C-5, **3** has an additional benzoyl group, assigned to C-10 due to the relative downfield signal of H-10 [δ = 6.33 (1H, d, J = 10.4 Hz)]. Direct evidence for this assignment was furnished by the presence of long-range heterocorrelation between H-10 and the benzoyl carbonyl carbon in the HMBC spectrum (Table **4**). Relative stereochemistry of **3** was determined to be the same as those of **1** and **2** according to its identical coupling constants and results from the ROESY experiment (Table **3**). Thus, compound **3** was determined to be 2α,4α,7β,9α,13α,15-hexahydroxy-5α,20-diacetoxy-10β-benzoxy-11(15→1)*abeo*taxa-11-ene, and given the trivial name taxuyunnanine U.

Compound **4** was isolated as a colorless amorphous solid with a molecular formula of $C_{28}H_{42}O_{12}$ shown by HRFABMS (*m/z* 569.2651, calcd: 569.2598). Analysis of the ^{1}H- and ^{13}C-NMR revealed that **4** is an opened 11(15→1)-*abeo*taxaxoid having a 4(20)-oxetane opened ring as in isolates **1 – 3**, but contrary to the quaternary C-4 carbon in **1 – 3** (around δ = 77 ppm), the C-4 of **4** is a protonated methine carbon (δ 44.1 ppm). The H-3 of **4** showed a doublet of doublet instead of a doublet, and the H_2 – 20 were two doublet of doublets instead of an AB doublet as found in **1 – 3**. Further evidence for **4** being an opened ring was furnished from the H-2/H-3/H-4/H_2 – 20 chain link observed in the ^{1}H-^{1}H COSY experiment. From its ^{1}H-NMR spectrum, **4** was shown to have four acetoxy groups, positioned at C-5, C-7, C-9 and C-13, respectively, based on the relative downfield proton signals of H-9 [δ = 6.34 (1H, d, J = 10.5 Hz), H-13 [δ = 5.91 (1H, t, J = 7.5 Hz)], H-7 [δ = 5.79 (1H, dd, J = 5.1, 11.6 Hz)] and H-5 [δ = 5.43 (1H, br d, J = 1.5 Hz)], and confirmed by the HMBC spectrum. The hydroxymethylene at C-4 was assigned to be β oriented based on the ROE correlation between H_2 – 20 and Me-19 in the 2D ROESY spectrum (Tab. **3**). Other chiral centers in **4** remained the same as those of **1 – 3** according to the observed ROEs. Compound **4** was therefore determined to be 2α,10β,15,20-tetrahydroxy-5α,7β,9α,13α-tetraacetoxy-11(15→1)*abeo*taxa-11-ene, and was given the trivial name taxuyunnanine V.

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Table **4** HMBC correlations of compounds **1 – 4** (500 MHz)

Proton	*1*[b]	*2*[a]	*3*[b]	*4*[a]
H-2	C-1, 3, 14, 15	C-8, 14, 15	C-1, 3, 14	C-1, 8, 14, 15
H-3	C-1, 2, 4, 7, 8, 19	C-4, 7, 8, 9, 19, 20	C-2, 4, 8, 20	C-1, 2, 4, 8, 19, 20
H-4				C-5, 8, 20
H-5	C-3, 7	C-3, 4, 7, OAc*	C-3, 4, 7, OAc*	C-3, 7, OAc*
H-6a	C-4	C-7, 8	C-7, 8	C-4, 5, 8
H-6b	C-7	C-7, 8		C-4, 5, 8
H-7	C-9, 19	C-6, 9, 19	C-6, 8, 9, 19	C-6, 8, 9, 19, OAc*
H-9	C-8, 10, 19	C-8, 10, 19	C-7, 8, 10, 19	C-7, 8, 10, 19, OAc*
H-10	C-1, 9, 11, 12	C-1, 9, 11, 12	C-1, 9, 11, 12, 1′	C-1, 9, 11, 12, 13
H-13	C-11, 12	C-11, 12	C-11, 12	C-11, 12, OAc*
H-14a	C-1, 11, 12, 15	C-1, 2, 13, 15	C-1, 2, 11, 12, 13, 15	C-1, 11, 12, 13, 15
H-14b	C-1, 13, 15	C-1, 2, 11, 12, 13, 15	C-1, 2, 13, 15	C-1, 2, 13, 15
CH_3-16	C-1, 15, 17	C-1, 15, 17	C-1, 15, 17	C-1, 15, 17
CH_3-17	C-1, 15, 16	C-1, 15, 16	C-1, 15, 16	C-1, 15, 16
CH_3-18	C-11, 12, 13	C-11, 12, 13	C-11, 12, 13	C-11, 12, 13
CH_3-19	C-3, 7, 8, 9	C-3, 7, 8, 9	C-3, 7, 8, 9	C-3, 7, 8, 9
H-20a	C-4, 5	C-4, 5, OAc*	C-4, 5, OAc*	C-4, 5
H-20b	C-4, 5	C-5, OAc*	C-5, OAc*	C-3, 4, 5
H-3′			C-1′, 2′, 3′, 5′	
H-4′			C-2′, 3′, 4′	
H-5′			C-3′	

* The carbonyl carbon of the acetoxy group.

[a] Data were obtained in pyridine-d_5.

[b] Data were obtained in CD_3OD.

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