Chemical Constituents from *Amentotaxus yunnanensis* and *Torreya yunnanensis*

Sheng-Hong Li,[†] Hong-Jie Zhang,*[,†,‡] Xue-Mei Niu,[†] Ping Yao,[‡] Han-Dong Sun,[†] and Harry H. S. Fong*[,‡]

State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, The Chinese Academy of Sciences, Kunming 650204, Yunnan, People's Republic of China, and Program for Collaborative Research in the Pharmaceutical Sciences, Department of Medicinal Chemistry and Pharmacognosy (M/C 877), College of Pharmacy, University of Illinois at Chicago, 833 S. Wood Street, Chicago, Illinois 60612

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In a chemical study of taxonomically related Taxaceae plants of Yunnan Province, China, seven compounds, including a new amentoflavone biflavonoid, 2,3-dihydro-7,7″-dimethoxyamentoflavone (**1**), were isolated from *Amentotaxus yunnanensis*, and 12 isolates were obtained from *Torreya yunnanensis*. From the latter plant, a new abietane diterpene, torreyayunnin (**7**), is reported for the first time. The known isolates from *A. yunnanensis* have been identified as sequoiaflavone (**3**), sotetsuflavone (**4**), 7,7″-dimethoxyamentoflavone (**5**), lutein, *β*-sitosterol, and sequoyitol. Amentoflavone (**2**), sotetsuflavone (**4**), sciadopitysin (**6**), 12-hydroxydehydroabietinol, meridinol, balanophonin, (+)-pinoresinol monomethyl ether, (+)-pinoresinol monomethyl ether glucoside, *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2- methoxyphenoxy}propane-1,3-diol, *threo*-1-(4-hydroxy-3-methoxyphenyl)-2- {4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}propane-1,3-diol, and (*E*)-2-butenedioic acid were identified as known isolates from *T. yunnanensis*. The presence of the amentoflavone biflavonoids (**1**, **3**−**5**) in *A. yunnanensis* supports its placement in the Taxaceae. The occurrence of the biflavonoid sotetsuflavone (**4**) in both *A. yunnanensis* and *T. yunnanensis* suggests that these two genera are closely related. The identification and structural elucidation of these isolates were based on spectral data analysis including 1D and 2D NMR.

Amentotaxus yunnanensis Li and *Torreya yunnanensis* Cheng et L. K. Fu are Taxaceae plants endemic to Yunnan Province, China.[1] Their taxonomic positions in the Taxaceae, however, are still in dispute.[2] Therefore, a comparative analysis of their phytochemical profile may be of value in resolving this taxonomic dilemma. Interestingly, the secondary chemistry of neither plant has been previously investigated. For the present study, the leaves and twigs of both plants were field collected and subjected to phytochemical investigation. As a result, seven compounds were isolated from *A. yunnanensis*, and 12 compounds were obtained from *T. yunnanensis*. The biflavonoid **1**, 2,3-dihydro-7,7″-dimethoxyamentoflavone, and the abietane diterpenoid, torreyayunnin (**7**), were determined to be new metabolites from *A. yunnanensis* and *T. yunnanensis*, respectively. The present paper describes the isolation and identification of these compounds, and their chemotaxonomic significance is also presented.

2,3-Dihydro-7,7″-dimethoxyamentoflavone (**1**), sequoiaflavone (**3**),[3] sotetsuflavone (**4**),[3] 7,7″-dimethoxyamentoflavone (**5**),[4] lutein,[5] *β*-sitosterol,[6] and sequoyitol[7] were isolated from the Et_2O extract of the air-dried leaves and twigs of *A. yunnanensis*. Workup of the EtOH extract of the air-dried leaves and twigs of *T. yunnanensis* yielded the abietane **7**, amentoflavone (**2**),[8] sotetsuflavone (**4**),[3] sciadopitysin (**6**),[9] 12-hydroxydehydroabietinol,[10,11] meridinol,[12] balanophonin,[13] (+)-pinoresinol monomethyl ether,[14] (+)-pinoresinol monomethyl ether glucoside,[15] *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2- methoxyphenoxy}propane-1,3-diol,[16] *threo*-1-(4-hydroxy-3-methoxyphenyl)-2- {4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}-propane-1,3-diol,[16] and (*E*)-2-butenedioic acid.[17] The structures of the known compounds were identified by comparison of their MS and ^1H and ^{13}C NMR data with those reported in the literature. Structural determination of the new compounds (**1** and **7**) was accomplished on the basis of spectral analysis, especially 2D NMR spectroscopy.

2,3-Dihydro-7,7″-dimethoxyamentoflavone (**1**) was isolated as a yellow powder. Its EIMS displayed a molecular ion as base peak at *m*/*z* 568, corresponding to a molecular formula of $C_{32}H_{24}O_{10}$, which was confirmed by HREIMS ($[M]^+$ *m*/*z* 568.1367, calcd 568.1369). The similarity of the NMR spectra of **1** (Table 1) to those of the biflavones, **2**−**6**, indicated that it is an amentoflavone derivative having two methoxy groups [δ_H 3.74 and 3.81 (each 3H, s) and δ_C 55.7 and 56.2 (each q)]. However, **1** differs from **2**−**6** by being composed of a flavanone and a flavone instead of two flavone units. A flavanone unit in **1** was demonstrated by upfield signals in the NMR spectra at δ_H 5.54 (1H, dd, J = 2.8, 13.2 Hz, H-2), δ_H 3.42 (1H, m, H-3a), δ_H 2.73 (1H, m, H-3b), δ_C 78.6 (d, C-2), and δ_C 42.1 (t, C-3), which were similar to those of **5**.[7] The C-5, -4′, -5″, and -4‴ in **1** were hydroxylated due to the existence of the HMBC correlations (Figure 2) of the phenolic hydroxyl signals at δ_H 12.10 (1H, s) to C-5, C-6, C-10; δ_H 9.56 (1H, s) to C-3′, C-4′, C-5′; δ_H 13.21 (1H, s) to C-5″, C-6″, C-10″; and δ_H 10.37 (1H, s) to C-3‴, C-4‴, C-5‴. The HMBC spectrum also assigned the two methoxy groups of **1** to C-7 and C-7″, respectively. The flavone unit in **1** was thus determined to be the same as that in **5**, and the flavanone unit as that of 7-*O*-methyl-2,3-dihydroamentoflavone, a compound previously reported from *Libocedrus bidwillii*.[18] The C-3′/C-8″ linkage between the flavanone unit and the flavone unit was confirmed by the HMBC interactions observed between H-2 [δ_H 5.54 (1H, dd, J = 2.8, 13.2 Hz)] and C-2′ (δ_C 131.2, d), and between H-2′ [δ_H 7.39 (1H, d, J = 2.1 Hz)] and C-8″ (δ_C 105.7, s). Accordingly, **1** was determined to be 2,3-dihydro-7,7″-dimethoxyamentoflavone.

Torreyayunnin (**7**) was obtained as pale yellow needles and was shown to have a molecular formula of $C_{20}H_{26}O_4$

* To whom correspondence should be addressed. Tel: (312)996-7868. Fax: (312)413-5894. E-mail: zhanghj@uic.edu and hfong@uic.edu.
[†] Kunming Institute of Botany.
[‡] University of Illinois at Chicago.

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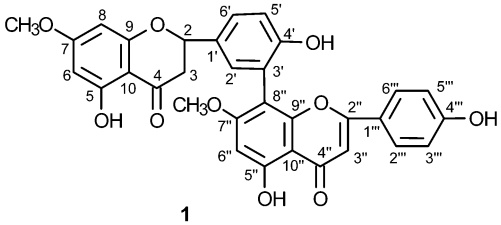

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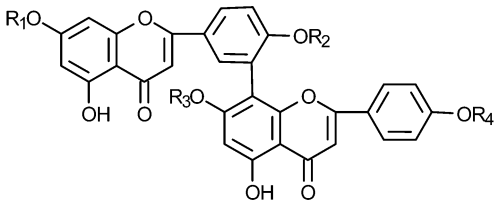


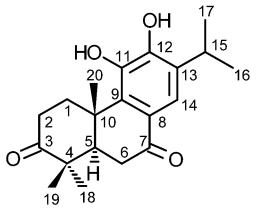
2 $R_1 = R_2 = R_3 = R_4 = H$

3 $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$

4 $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$

5 $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$

6 $R_1 = R_2 = R_4 = CH_3$, $R_3 = H$



7

Figure 1. Structures of compounds from *A. yunnanensis* and *T. yunnanensis*.

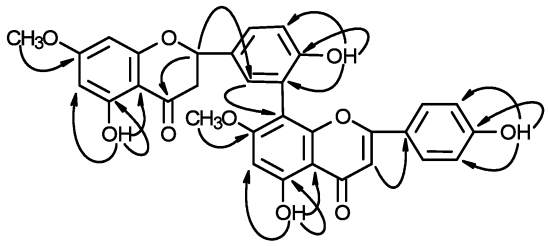


Figure 2. Selected HMBC correlations of **1**.

by HREIMS analysis of the molecular ion (base peak) at *m*/*z* 330 (found *m*/*z* 330.1828, calcd 330.1831). The NMR spectra of **7** (Table 2) showed the presence of a pentasubstituted benzene moiety [δ_H 7.53 (1H, s) and δ_C 117.5 (d), 125.6 (s), 134.4 (s), 137.7 (s), 144.0 (s), 148.5 (s)], an isopropyl residue [δ_H 3.29 (1H, sept, J = 6.8 Hz), 1.18 (3H, d, J = 6.8 Hz), 1.20 (3H, d, J = 6.8 Hz) and δ_C 27.4 (d), 23.0 (q), 22.9 (q)], and three tertiary methyls [δ_H 1.14 (6H, s), 1.48 (3H, s) and δ_C 27.2 (q), 21.1 (q), 18.0 (q)], indicative of **7** being an abietane type diterpenoid with an aromatic C-ring. Two keto carbonyl carbon signals were observed in the ^{13}C NMR and DEPT spectra of **7** at δ_C 216.0 and 196.9, respectively. The carbonyl carbon at δ_C 216.0 was positioned at C-3 on the basis of its HMBC correlations (Figure 3) to H-1, -2, -18, and -19. The significant upfield shift of the carbonyl carbon at δ_C 196.9 suggested a conjugation with the aryl group, which was confirmed by the IR and UV spectral data. The carbonyl absorption at 1696 cm^{-1} in the IR spectrum also suggested the carbonyl to be conjugated. In addition, employing Woodward's

Table 1. ^{1}H and ^{13}C NMR Data of **1** (DMSO-d_6, δ in ppm)

δ_H (multiplicity, J in Hz)[a]		δ_C[b]			
H-2	5.54 (1H, dd, 2.8, 13.2)	C-2	78.6 d	C-2″	163.9 s
H-3a	3.42 (1H, m)	C-3	42.1 t	C-3″	102.3 d
H-3b	2.73 (1H, m)	C-4	196.7 s	C-4″	182.3 s
H-6	6.05 (1H, d, 2.8)	C-5	163.1 s	C-5″	161.0 s
H-8	6.06 (1H, d, 2.8)	C-6	94.6 d	C-6″	95.3 d
H-2′	7.39 (1H, d, 2.1)	C-7	167.3 s	C-7″	162.6 s
H-5′	7.01 (1H, d, 8.4)	C-8	93.6 d	C-8″	105.7 s
H-6′	7.42 (1H, dd, 2.0, 8.4)	C-9	162.9 s	C-9″	153.4 s
H-3″	6.83 (1H, s)	C-10	102.5 s	C-10″	104.0 s
H-6″	6.62 (1H, s)	C-1′	128.5 s	C-1‴	121.2 s
H-2‴,	7.58 (1H, dd, 3.6, 8.4)	C-2′	131.2 d	C-2‴	128.3 d
H-3‴	6.78 (1H, dd, 3.2, 8.8)	C-3′	118.6 s,	C-3‴	115.7 d
H-5‴	6.78 (1H, dd, 3.2, 8.8)	C-4′	155.9 s	C-4‴	161.1 s
H-6‴	7.58 (1H, dd, 3.6, 8.4)	C-5′	115.4 d	C-5‴	115.7 d
5-OH	12.10 (1H, s)	C-6′	127.8 d	C-6‴	128.3 d
4′-OH	9.56 (1H, s)	7-OCH_3	55.7 q	7″-OCH_3	56.2 q
5″-OH	13.21 (1H, s)				
4‴-OH	10.37 (1H, s)				
7-OCH_3	3.74 (3H, s)				
7″-OCH_3	3.81 (3H, s)				

[a] Recorded at 400 MHz with reference to the solvent signal. [b] Recorded at 100 MHz with reference to the solvent signal.

Table 2. ^{1}H and ^{13}C NMR Data of **7** (acetone-d_6, δ in ppm)

position	δ_H (multiplicity, J in Hz)[a]	δ_C[b]
1	2.01 (1H, m, H-1α)	36.4 t
	3.37 (1H, m, H-1β)	
2	2.60 (2H, m, H-2α and 2β)	34.9 t
3		216.0 s
4		47.6 s
5	2.47 (1H, m)	50.5 d
6	2.43 (1H, m, H-6α)	36.5 t
	2.64 (1H, m, H-6β)	
7		196.9 s
8		125.6 s
9		137.7 s
10		39.7 s
11		144.0 s
12		148.5 s
13		134.4 s
14	7.53 (1H, s)	117.5 d
15	3.29 (1H, sept, 6.8)	27.4 d
16	1.18 (3H, d, 6.8)	23.0 q
17	1.20 (3H, d, 6.8)	22.9 q
18	1.14 (3H, s)	27.2 q
19	1.14 (3H, s)	21.1 q
20	1.48 (3H, s)	18.0 q

[a] Recorded at 400 MHz with reference to the solvent signal. [b] Recorded at 100 MHz with reference to the solvent signal.

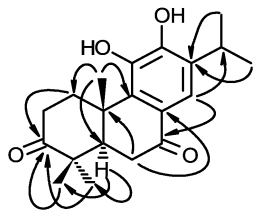


Figure 3. Selected HMBC correlations of **7**.

empirical rules, a value of λ_{max} 283 nm of UV absorption was calculated for the substituted benzoyl group, which was in good agreement with the observed value of 280.5 nm. This carbonyl carbon was assigned to C-7 on the basis of its HMBC long-range correlations to H_2-6 [δ_H 2.43, 2.64 (each 1H, m)] and to the aromatic proton at δ_H 7.53 (1H,

s), which, in turn, determined the proton at δ_H 7.53 (1H, s) as H-14. Further, the HMBC correlation from the aromatic proton to the carbon signal at δ_C 27.4 (d) positioned the isopropyl group at C-13. Two structurally related compounds, (+)-(5*R*,10*S*)-11,12,14-trihydroxy-8,11,13-abietatriene-3,7-dione and taxusabietane A, reported from *Salvia candelabrum*[19] and *Taxus mairei*[20] respectively, exhibited very similar NMR spectral data. Compound **7** differs from (+)-(5*R*,10*S*)-11,12,14-trihydroxy-8,11,13-abietatriene-3,7-dione only by the absence of the 14-OH, and it differs from taxusabietane A by the presence of a hydroxyl instead of a methoxyl group at C-12. Thus, **7** was established as 11,12-dihydroxy-8,11,13-abietatriene-3,7-dione and was given the trivial name of torreyayunnin.

The isolation of the amentoflavones **1**, **3**, **4**, and **5** from *A. yunnanensis* represents the first report of biflavonoids from this genus. A previous investigation of a related species, *A. argotaenia*, showed it to be devoid of this type of compound.[2,21,22] In fact, Ma et al.[2] questioned the placement of *Amentotaxus* along with the genera *Taxus*, *Pseudotaxus*, and *Torreya* in the Taxaceae on the basis of the absence of amentoflavones in their sample of *A. argotaenia*. On the contrary, our data showed not only the existence of amentaflavones (**1**, **3**, **4**, and **5**) in our sample of *A. yunnanensis* but that these compounds occurred as major constituents. In the case of *T. yunnanensis*, our discovery of the presence of amentoflavones (**2**, **4**, and **6**) is consistent with previous studies.[2,10,14,23−27] Interestingly, taxane diterpenes such as paclitaxel (Taxol), 1β-baccatin I, 9-dihydro-13-acetylbaccatin III, baccatin III, and 7-xylosyl-10-deacetylpaclitaxel, which are major taxoids found in most yew species, were neither isolated nor detected by TLC analysis of the Et_2O or EtOH extracts of our *A. yunnanensis* and *T. yunnanensis* samples. This lack of taxanes, coupled with the occurrence of **4** and structurally related amentoflavone biflavonoids in both of these plants, supports the position that the genera *Amentotaxus* and *Torreya* are taxonomically closer to each other than to the genus *Taxus*.[28]

Experimental Section

General Experimental Procedures. 1D and 2D NMR experiments were performed either on a Bruker AM-400 or on a DRX-500 spectrometer. 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 on 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 a Perkin-Elmer model 241 polarimeter. Column chromatography was performed either on Si gel (200−300 mesh, Qingdao Marine Chemical, China), Si gel H (10−40 μ, Qingdao Marine Chemical, China), or MCI gel CHP20P (75-150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan). Preparative HPLC was performed on a Shimadzu instrument (column: Shim-pack PRC-ODS (K), 5 μm, 250 × 30 mm; solvents: 33% CH_3OH-H_2O; UV detection: 330 nm; flow rate: 20 mL/min). Fractions were monitored by TLC, and spots were visualized by heating Si gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant Materials. The leaves and twigs of *A. yunnanensis* Li (Taxaceae) were collected in the Wenshan Prefecture of Yunnan Province, China, in Feburary 1999, and identified by Professor Hang Sun of Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming, China. The leaves and twigs of *T. yunnanensis* Cheng et L. K. Fu (Taxaceae) were collected in the Lijiang Prefecture of Yunnan Province, China, in May 1999, and identified by Professor Zhe-Kun Zhou of Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming, China. Voucher specimens of both collections (*A. yunnanensis*: No. KIB 99-02-02 Sun; *T. yunnanensis*: No. KIB 99-0508 Zhou) have been deposited at the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, the Chinese Academy of Sciences.

Extraction and Isolation. The air-dried and ground leaves and twigs of *A. yunnanensis* (6.0 kg) were extracted with Et_2O (15 L × 4) at room temperature (3 × 48 h) to yield an Et_2O extract (300 g). The Et_2O extract was absorbed on Si gel (500 g) and chromatographed on a pre-packed Si gel (1.5 kg) column using gradient elution with $CHCl_3$ and increasing concentrations of Me_2CO to afford five fractions [$CHCl_3-Me_2CO$, 10:0 (eluate F-1, each 10.0 L), 9:1 (eluate F-2, 8.0 L), 8:2 (eluate F-3, 8.0 L), 7:3 (eluate F-4, 8.0 L), 0:100 (eluate F-5, 5.0 L), respectively]. β-Sitosterol (30 mg) and sequoyitol (10 mg) were obtained from fractions F-1 and F-5, respectively, by direct crystallization. Fraction F-2 was rechromatographed on a Si gel column eluting with petroleum ether−Me_2CO (2:1) and subsequently on MCI gel CHP20P eluting with aqueous Me_2CO (60%) to yield lutein (9 mg) as red needles. Fraction F-3 was subjected to further Si gel column chromatography with increasing amounts of MeOH in $CHCl_3$ to afford four fractions [$CHCl_3$−MeOH, 95:5 (eluate F-3-1, 5.0 L), 90:10 (eluate F-3-2, 5.0 L), 80:20 (eluate F-3-3, 5.0 L), 50:50 (eluate F-3-4, 3.0 L), respectively]. 2,3-Dihydro-7,7″-dimethoxyamentoflavone (**1**, 107 mg), sequoiaflavone (**3**, 15 mg), sotetsuflavone (**4**, 20 mg), and 7,7″-dimethoxyamentoflavone (**5**, 1.2 g) were obtained from fractions F-3-1, -2, -3, and -4, respectively, after crystallization with *N*,*N*-dimethylformamide (DMF).

The air-dried leaves and twigs of *T. yunnanensis* (25.0 kg) were milled and macerated in EtOH at room temperature (3 × 48 h) to yield an EtOH extract, which was concentrated and subsequently partitioned with petroleum ether (4 × 10 L) and EtOAc (4 × 10 L) to afford an EtOAc extract (600 g). The EtOAc extract was adsorbed on 900 g of Si gel and chromatographed on a prepacked Si gel (2.0 kg) column, eluting with $CHCl_3-Me_2CO$ of increasing polarity, to afford five fractions [$CHCl_3-Me_2CO$, 10:0 (eluate F-I, 15.0 L), 9:1 (eluate F-II, 10.0 L), 8:2 (eluate F-III, 10.0 L), 7:3 (eluate F-IV, 10.0 L), 0:100 (eluate F-V, 8.0 L), respectively]. Crude meridinol (24.5 g) was obtained from fractions F-III and F-IV by fractional crystallization. A portion of the crude meridinol (1.5 g) was recrystallized to yield 770 mg of pure isolate. Fraction F-I was repeatedly subjected to Si gel CC using $CHCl_3-Me_2CO$, petroleum ether−Me_2CO, and petroleum ether−$CHCl_3$−MeOH as eluting systems to afford 12-hydroxydehydroabietinol (304 mg), meridinol (6 mg), balanophonin (217 mg), and (+)-pinoresinol monomethyl ether (2.4 g). Fraction F-II was rechromatographed on a Si gel (500 g) column, eluting with $CHCl_3$−EtOAc and $CHCl_3$−*i*-PrOH to yield sciadopitysin (**6**, 95 mg) and torreyayunnin (**7**, 11 mg), respectively. Fraction F-III was chromatographed on a Si gel (500 g) column eluting with $CHCl_3$−*i*-PrOH to afford sotetsuflavone (**4**, 20 mg) and a mixture (120 mg) of two compounds. The mixture was further separated by chromatography on preparative HPLC using H_2O−MeOH, 67:33, as eluent to yield *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}-propane-1,3-diol (18 mg) and *threo*-1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}propane-1,3-diol (22 mg). Amentoflavone (**2**, 1.9 g) was obtained from fraction F-IV, which was chromatographed over a Si gel (300 g) column and eluted with $CHCl_3$−MeOH, 9:1. Workup of fraction F-V in the same manner as fraction F-IV yielded (+)-pinoresinol monomethyl ether glucoside (5.5 g).

2,3-Dihydro-7,7″-dimethoxyamentoflavone (1): yellow powder; mp > 290 °C; $[\alpha]_D^{24.5}$ +5.10° (*c* 0.29, C_5H_5N); UV (H_2O) λ_{max} 221, 284 nm; IR (KBr) ν_{max} 3428, 1651, 1601, 1573, 1498, 1442, 1372, 1335, 1291, 1242, 1204, 1178, 1155, 1117, 1087, 1018, 935, 834 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; EIMS *m*/*z* 568 $[M]^+$ (100), 551 (4), 403 (26), 389 (24), 167 (11), 121 (16); HREIMS *m*/*z* 568.1367 (calcd for $C_{32}H_{24}O_{10}$ 568.1369).

Torreyayunnin (7): pale yellow needles (from acetone); mp 232 °C; $[\alpha]_D^{19.8}$ +87.09° (*c* 0.24, MeOH); UV (MeOH) λ_{max}

(log ϵ) 280.5 (4.43) nm; IR (KBr) ν_{max} 3400, 3200, 2971, 2880, 1696, 1654, 1601, 1565, 1463, 1385, 1364, 1313, 1225, 1188, 1150, 1112, 1046, 998, 936, 886, 784, 688, 657, 627, 506, 436 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2; EIMS *m/z* 330 $[M]^+$ (100), 315 (30), 297 (3), 287 (16), 273 (36), 259 (11), 245 (15), 233 (25), 219 (25), 205 (12), 179 (7), 161 (6), 145 (7), 128 (14), 115 (17), 91 (14), 77 (12), 69 (19), 55 (42); HREIMS *m/z* 330.1828 (calcd for $C_{20}H_{26}O_4$ 330.1831).

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Supporting Information Available: NMR and MS data of all known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wu, Z. Y. *Index Florae Yunnanensis (Tomus I)*; the People's Publishing House: Yunnan, China, 1984; pp 24−26.
(2) Ma, Z. W.; He, G. F.; Yin W. F. *Acta Phytotax. Sin.* **1985**, *23*, 192−195.
(3) Geiger, H.; Pfleiderer, W. De G. *Phytochemistry* **1971**, *10*, 1936−1938.
(4) Gu, Y.-L.; Xu, Y.-M.; Fang, S.-D.; He, Q.-M. *Acta Bot. Sin.* **1990**, *32*, 631−636.
(5) Buchecker, R.; Hamm, P.; Eugster, C. H. *Helv. Chim. Acta* **1974**, *57*, 631−656.
(6) Kalinowska, M.; Nes, W. R.; Crumley, F. G.; Nes, W. D. *Phytochemistry* **1990**, *29*, 3427−3434.
(7) Sultana, N.; Hartley T. G.; Waterman, P. G. *Phytochemistry* **1999**, *50*, 1249−1253.
(8) Markham, K. R.; Sheppard, C.; Geiger, H. *Phytochemistry* **1987**, *26*, 3335−3337.
(9) Miura, H.; Kihara, T.; Kawano, N. *Chem. Pharm. Bull.* **1969**, *17*, 150−154.
(10) Fukushima, I.; Sayama, Y.; Kyogoku K.; Murayama, H. *Agric. Biol. Chem.* **1968**, *32*, 1103−1107.
(11) Ulubelen, A.; Topcu, G. *Phytochemistry* **1992**, *31*, 3949−3951.
(12) Amaro-Luis, J. M.; Fronczek, F. R.; Massanet, G. M.; Pando, E.; Rodriguez-Luis, F.; Watkins, S. F.; Zubia, E. *Phytochemistry* **1988**, *27*, 3933−3935.
(13) Haruna, M.; Koube, T.; Ito, K.; Murata, H. *Chem. Pharm. Bull.* **1982**, *30*, 1525−1527.
(14) Cheng, R. T.; Zhang, Y. H.; Fang, S. D. *Zhongcaoyao* **1997**, *28*, 707−709.
(15) Chiba, M.; Hisada, S.; Nishibe, S.; Thieme, H. *Phytochemistry* **1980**, *19*, 335−336.
(16) Miki, K.; Takehara, T.; Sasaya, T.; Sakakibara, A. *Phytochemistry* **1980**, *19*, 449−453.
(17) Braun, S. *Org. Magn. Reson.* **1978**, *11*, 197−203.
(18) Markham, K. R.; Franke, A.; Molloy, B. P. J.; Webby, R. F. *Phytochemistry* **1990**, *29*, 501−507.
(19) Salvador, C.; Jose, I.; Francisco, S.-F.; Albert, V. *Phytochemistry* **1988**, *27*, 221−224.
(20) Yang, S. J.; Fang, J. M.; Cheng, Y. S. *Phytochemistry* **1998**, *49*, 2037−2043.
(21) Ma, Z. W.; He, G. F.; Yin W. F. *Acta Bot. Sin.* **1984**, *26*, 340−342.
(22) Ma, Z. W.; He, G. F.; Yin W. F. *Acta Phytotax. Sin.* **1986**, *24*, 443−446.
(23) Zhao, Y.; Nookandeh, A.; Schneider, B.; Sun, X. F.; Schmitt, B.; Stockigt, J. *J. Chromatogr. A* **1999**, *837*, 83−91.
(24) He, G. F.; Ma, Z. W.; Yin W. F. *Acta Pytotax. Sin.* **1983**, *21*, 433−435.
(25) He, G. F.; Ma, Z. W.; Yin W. F.; Zhang, S. D.; Lin X. Y.; Shen, F. L.; Zheng, Q. T. *Acta Bot. Sin.* **1985**, *27*, 300−303.
(26) Beatrice, G.; Francesco, G.; Virginia, L.; Domenico, M.; Raffaele, R.; Claudio, V.; He, G. F.; Ma, Z. W.; Yin, W. F. *Tetrahedron* **1999**, *55*, 11385−11394.
(27) Sayama, Y.; Kyogoku K.; Murayama, H. *Agric. Biol. Chem.* **1971**, *35*, 1068−1073.
(28) Edward, A. C. *Bot. Rev.* **1998**, *64*, 291−322.

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