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贡山八角枝叶化学成分研究

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摘　要:为研究贡山八角枝叶的化学成分,我们利用色谱法对贡山八角(*Illicium wardii* A. C. Smith)枝叶 95% 乙醇提取物中的化学成分进行分离。利用核磁共振、质谱、红外等方法对分离得到的单体化合物进行结构鉴定,从贡山八角枝叶中分离得到了 15 个化合物,分别是 β-谷甾醇(**1**)、二十六烷(**2**)、红花八角醇(**3**)、三十四烷醇(**4**)、异鼠李素-3-*O*-β-D-芸香糖苷(**5**)、acernikol(**6**)、subamone(**7**)、苔色酸甲酯(**8**)、扁柏脂内酯(**9**)、厚朴酚(**10**)、原儿茶酸(**11**)、异红花八角醇(**12**)、vitrifol A(**13**)、右旋二氢去氢双松柏醇(**14**)、左旋马尾松树脂醇(**15**)。其中化合物 **2** ~ **15** 首次从该植物中分离得到,化合物 **7** 和 **15** 为首次从该科植物中分离得到。

关键词:贡山八角;化学成分;八角科;木质素;单萜

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Chemical Constituents of Branches and Leaves of *Illicium wardii* A. C. Smith

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Abstract: To investigate chemical constituents of the branches and leaves of *Illicium wardii* A. C. Smith. Chemical constituents were isolated using column chromatography from 95% ethanol extracts of the branches and leaves of *I. wardii*. Their structures were elucidated by NMR, IR and MS techniques. Fifteen compounds were obtained and identified as β-sitosterol (**1**), hexacosane (**2**), dunnianol (**3**), tetratriacontanol (**4**), isorhamnetin-3-*O*-β-D-rutinoside (**5**), acernikol (**6**), subamone (**7**), methyl-β-orsellinate (**8**), hinokinin (**9**), magnolol (**10**), protocatechuic acid (**11**), isodunnianol (**12**), vitrifol A (**13**), (+)-dihydrodehydrodiconiferyl alcohol (**14**) and (-)-massoniresinol (**15**). Compounds **2**-**15** were obtained from this plant firstly, and compounds **7** and **15** were found from Illiciaceae family firstly.

Key words: *Illicium wardii*; chemical constituent; Illiciaceae; lignan; monoterpene

Introduction

Illicium wardii A. C. Smith belongs to Illicium genus, which is the only genus of Illiciaceae family containing about 50 species globally. There are 28 species and two variants distributed in the southwest, south and east of China[1]. Plants from Illicium genus are evergreen trees or shrubs and some of them are used to treat rheumatism, traumatic injury and stomach cold vomiting in Traditional Chinese Medicine (TCM)[2]. However, the phytochemical investigation of *I. wardii* is seldom reported. Up to now, only fourteen compounds isolated from the fruits of the plant have been reported by Min Y, *et al*[3] and Gao YP, *et al*[4]. As a continuation of our phytochemical studies of Illicium genus, we focused on the isolation and structural identification of chemical constituents from the branches and leaves of *I. wardii* and resulted in the isolation of fifteen compounds, which were assigned as β-sitosterol (**1**), hexacosane (**2**), dunnianol (**3**), tetratriacontanol (**4**), isorhamnetin-3-*O*-β-D-rutinoside (**5**), acernikol (**6**), subamone (**7**), methyl-β-orsellinate (**8**), hinokinin (**9**), magnolol (**10**), protocatechuic acid (**11**), isodunnianol (**12**), vitrifol A (**13**), (+)-dihydrodehydrodiconiferyl alcohol (**14**) and (-)-massoniresinol (**15**), respectively. Compounds **2**-**15** were obtained from this plant firstly, and compounds **7** and **15** were isolated from Illiciaceae family firstly.

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Materials and Methods

Plant materials

The plants of *I. wardii* were collected in Nujiang county of Yunnan province, China in August 2011 and identified by Prof. Yuanchuan Zhou, the director of Nujiang Nationality Medicine Plants Institution.

Experimental apparatus and materials

Melting points were measured by a RY-1 micro-melting point apparatus without correction. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter. IR spectra was obtained on a Bruker FTIR Vector 22 spectrometer with KBr pellets. Normal phase silica gel (200-300 mesh, Yantai), MCI gel (CHP20P 75-150 μM, Mitsubishi Chemical Co.) and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden) were used for column chromatography, and precoated silica $HSGF_{254}$ (10-40 μm, Yantai) plates were used for TLC analysis. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker DRX-500 spectrometer for ^1H NMR at 500 MHz and ^{13}C NMR, DEPT at 126 MHz. ESI-MS analyses were carried out on Agilent-1100-LC/MSD-Trap (ESI-MS) and Agilent Micro-Q-Tof in *m/z*. HPLC and preparative HPLC analyses were performed with SHIMADZU LC-2010AHT, Agilent Technologies 1200 series and SHIMADZU LPD-20A. Petroleum ether/ethyl acetate and methylene chloride/methanol (different proportions) were used in the chromatographic solvent system.

Extraction and Isolation

The air-dried branches and leaves of *I. wardii* (17.4 kg) were extracted for three times with 95% EtOH by reflux extraction (2 h/time). The extract was further concentrated under reduced pressure to yield 1.7 kg residue. The residue was reconstituted in H_2O and liquid-liquid extracted successively with petroleum ether (PE), methylene chloride (CH_2Cl_2) and ethyl acetate (EtOAc) to yield 300.0 g, 270.0 g and 100.0 g, respectively.

PE fraction (100.0 g) was chromatographed on silica gel column eluting with PE: EtOAc (100∶0-0∶100, v/v) to obtain eight subfractions (a-h). Compound 2 (15.0 mg) was obtained from Fr. a. Compounds **1** (100.0 mg), **12** (10.0 mg) and **3** (40.0 mg) were obtained from Fr. a, Fr. e and Fr. j, respectively by recrystallization.

CH_2Cl_2 fraction was subjected to silica gel column with gradient CH_2Cl_2: MeOH (100∶0-2∶1, v/v) as eluents and eight subfractions (i-p) were obtained. Fr. i, Fr. l and Fr. m were applied to MCI gel column chromatography (CH_3OH: H_2O, 9∶1, v/v) firstly, then some white powder was obtained from Fr. l, to yield compound **4** (35 mg) by purification. Fr. i was subjected to a series of chromatographic columns, such as silica gel column, Sephadex LH-20, to obtain three subfractions Fr. i-1-Fr. i-3. And Fr. i-1 and Fr. i-3 were subjected to preparative HPLC (RP_{18}, 210 nm), yielded compound **7** (17.0 mg, 30% CH_3CN as eluents) from Fr. i-1, and compounds **8** (7.0 mg, 75% MeOH), **9** (3.0 mg, 75% MeOH) and **10** (3.0 mg, 85% MeOH) were obtained from Fr. i-3. Fr. m was subjected to preparative HPLC (RP_{18}, 210 nm, 45% MeOH), and to yield **5** (30.0 mg) and **6** (25.0 mg).

EtOAc fraction (100 g) was subjected to silica gel column with the gradient CH_2Cl_2: MeOH (100∶0-2∶1, v/v) as eluents and **9** subfractions (q-y) were obtained. Fr. s was subjected to a series of chromatographic columns, such as silica gel column, Sephadex LH-20 and preparative HPLC (RP_{18}, 210 nm) to yield compounds **11** (50.0 mg, 20% MeOH) and **13** (16.0 mg, 20% MeOH), **14** (120.0 mg, 40% MeOH) and **15** (35.0 mg, 40% MeOH).

Structural identification

Compound 1 Colorless needle crystal (MeOH), mp 136-138 ℃. Compound **1** exhibited the same Rf value with the standard β-sitosterol by TLC detection in three different eluents, and the melting point of the mixture didn't vary; It became purple under 105 ℃ by vanillin-sulfuric acid color reaction; Meanwhile, the result of Liebermann-Berchard reaction was positive. IR (υKBr max, cm^{-1}): 3445 (OH), 2978 (CH_3), 2868 (CH_2), 1650 (C=C), 1465 (CH_3 + CH_2), 1380, 1165 (isopropyl), 1060 (C-*O*-). The above data was in accordance with those reported in the literature[5], hence compound **1** was identified as β-sitosterol.

Compound 2 White power (CH_2Cl_2), $C_{26}H_{54}$, ESI-MS (positive): *m/z* 389 [M + Na]$^+$, ESI-MS (negative): *m/z* 365 [M-H]$^-$; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.26 (54H, m, H-2 ~ 25), 0.88 (6H, t, J = 7.0 Hz, H-1, 26); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.1 (C-1, 6), 22.7 (C-2, 25), 29.4 (C-4, 23), 29.7 (C-5, 22), 29.7 (C-6 ~ C-21), 31.9 (C-3, 4). The NMR data was in accordance with those reported in the literature[6], hence compound **2** was identified as hexacosane.

Compound 3 White crystal (MeOH), $C_{27}H_{26}O_3$, ESI-MS (positive): *m/z* 421 [M + Na]$^+$, ESI-MS (negative): *m/z* 397 [M-H]$^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 7.09 (2H, d, J = 1.9 Hz, H-3′, 3″), 7.07 (2H, brs, H-3, 5), 7.02 (2H, dd, J = 8.2, 2.2 Hz, H-5′, 5″), 6.87 (2H, d, J = 8.2 Hz, H-6′, 6″), 6.03 ~ 5.90 (3H, m, H-8, 8′, 8″), 5.11 ~ 4.97 (6H, m, H-9, 9′, 9″), 3.39 (2H, d, J = 6.7 Hz, H-7), 3.34 (4H, J = 6.6 Hz, H-7′, 7″); ^{13}C NMR (126 MHz, CD_3OD) δ: 39.1 (C-7′, 7″), 39.1 (C-7), 114.4 (C-9′, 9″), 114.6 (C-9), 115.8 (C-6″), 126.2 (C-2′, 2″), 127.6 (C-2, 6), 128.6 (C-5′, 5″), 130.8 (C-3, 5), 131.6 (C-3′, 3″), 131.7 (C-4′, 4″), 132.3 (C-4), 137.9 (C-8), 138.0 (C-8′, 8″), 149.1 (C-1), 151.9 (C-1′, 1″). The NMR data was in accordance with those reported in the literature[7], hence compound 3 was identified as dunnianol.

Compound 4 White amorphous powder (CH_2Cl_2), $C_{34}H_{70}O$, ESI-MS (positive): *m/z* 517 [M + Na]$^+$, ESI-MS (negative): *m/z* 493 [M-H]$^-$; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.64 (2H, t, J = 6.7 Hz, H-1), 1.25 (29H, brs, H-2 ~ H-33), 0.88 (3H, t, J = 6.3 Hz, H-34); ^{13}C NMR (126 MHz, $CDCl_3$): 14.1 (C-34), 22.7 (C-33), 25.7 (C-3), 29.4 (C-31), 29.6 (C-4 ~ C-30), 31.9 (C-32), 32.8 (C-2), 63.1 (C-1). The NMR data was in accordance with those reported in the literature[8], hence compound **4** was identified as tetratriacontanol.

Compound 5 Yellow needle crystal (MeOH), $C_{28}H_{32}O_{16}$, ESI-MS (positive): *m/z* 647 [M + Na]$^+$, ESI-MS (negative): *m/z* 623 [M-H]$^-$; Molish reation and HCl-Mg reation showed positive result. The aglycone is isorhamnetin by hydrolysis, and the glycosyl is composed of glucose and rhamnose by paper chromatography detection. ^{1}H NMR (500 Hz CD_3OD) δ: 7.94 (1H, d, J = 1.9 Hz, H-2′), 7.62 (1H, dd, J = 2.0 Hz, 8.5 Hz, H-6′), 6.91 (1H, d, J = 8.5 Hz, H-5′), 6.19 (1H, d, J = 2.0 Hz, H-6), 6.44 (1H, d, J = 2.0 Hz, H-8), 5.20 (1H, d, J = 7.4 Hz, H-1″), 4.52 (1H, d, J = 1.3 Hz, H-1‴), 3.94 (3H, s, CH_3O-3′), 3.81 (1H, dd, J = 11.1, 0.5 Hz, H_a-6″), 3.61 ~ 3.25 (11H, m, H-1″ ~ 5″, H-6″, H-1‴ ~ 5‴), 1.10 (3H, d, J = 6.3 Hz, H-6″); ^{13}C NMR (101 MHz, CD_3OD) δ: 16.6 (C-6‴), 55.3 (CH_3O-3′), 67.1 (C-6″), 68.4 (C-5‴), 70.2 (C-2‴), 70.6 (C-3‴), 70.8 (C-4″), 72.4 (C-4‴), 74.5 (C-2″), 75.9 (C-5″), 76.8 (C-3″), 101.0 (C-1‴), 101.1 (C-8), 103.1 (C-6), 103.8 (C-1″), 103.9 (C-10), 113.1 (C-2′), 114.7 (C-5′), 121.6 (C-6′), 122.6 (C-1′), 134.0 (C-3), 146.9 (C-4′), 149.5 (C-3′), 157.1 (C-2), 157.3 (C-9), 161.4 (C-5), 166.2 (C-7), 177.7 (C-4). The NMR data was in accordance with those reported in the literature[9], hence compound **5** was identified as isorhamnetin-3-*O*-β-D-rutinoside.

Compound 6 White amorphous powder (MeOH), $C_{31}H_{38}O_{11}$, ESI-MS (positive): *m/z* 609 [M + Na]$^+$, ESI-MS (negative): *m/z* 585 [M-H]$^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 6.96 (1H, s, H-2″), 6.76 (1H, d, J = 8.0 Hz, H-6″), 6.74 (2H, s, H-2, 5″), 6.70 (1H, s, H-6), 6.70 (2H, s, H-2′, 6′), 5.54 (1H, m, H-7′), 4.90 (1H, d, J = 5.2 Hz, H-7″), 4.24 (1H, m, H-8″), 3.86 (3H, s, CH_3O-3), 3.81 (3H, s, CH_3O-3″), 3.78 (6H, s, CH_3O-3′, 5′), 3.75 (2H , m, H-9′), 3.59 (2H, m, H-9″), 3.57 (2H, m, H-9), 3.46 (1H, m, H-8′), 2.62 (2H, t, J = 7.8 Hz, H-7), 1.81 (2H, m, H-8); ^{13}C NMR (101 MHz, CD_3OD) δ: 32.9 (C-7), 35.8 (C-8), 55.7 (C-8′), 56.4 (CH_3O-3″), 56.7 (CH_3O-5′, 3′), 56.9 (CH_3O-3), 61.7 (C-9″), 62.3 (C-9), 65.1 (C-9′), 74.1 (C-7″), 87.4 (C-8″), 88.7 (C-7′), 103.9 (C-2′), 104.0 (C-6′), 111.4 (C-2″), 114.2 (C-2), 115.8 (C-5″), 118.0 (C-6), 120.7 (C-6″), 129.5 (C-5), 133.7 (C-1″), 136.3 (C-4′), 137.2 (C-1), 145.3 (C-3), 147.0 (C-4″), 147.5 (C-4), 148.7 (C-3″), 154.6 (C-3′,

5′); The NMR data was in accordance with those reported in the literature[10], hence compound **6** was identified as acernikol.

Compound 7 Colorless oil (MeOH), $C_{10}H_{16}O_2$, ESI-MS (positive): *m/z* 191 $[M+Na]^+$, ESI-MS (negative): *m/z* 167 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 6.74 (1H, s, H-2), 4.31 (1H, d, J = 9.6 Hz, H-7), 2.39 (1H, dd, J = 16.0, 3.6 Hz, H-5b), 2.20 (1H, m, H-4, 5a), 1.91 (1H, m, H-6), 1.76 (3H, s, CH_3-3), 0.98 (3H, d, J = 6.8 Hz, CH_3-6), 0.92 (3H, d, J = 6.8 Hz, CH_3-4); ^{13}C NMR (126 MHz, CD_3OD) δ: 15.36 (CH_3-3), 16.76 (CH_3-4), 20.88 (CH_3-6), 27.33 (C-4), 37.27 (C-5), 51.24 (C-6), 69.47 (C-7), 135.44 (C-2), 151.91 (C-3), 202.39 (C-1). The NMR data was in accordance with those reported in the literature[11], hence compound **7** was identified as subamone.

Compound 8 Colorless crystal (MeOH), $C_{10}H_{12}O_4$, ESI-MS (positive): *m/z* 219 $[M+Na]^+$, ESI-MS (negative): *m/z* 195 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 6.21 (1H, s, H-5), 3.89 (3H, s, CH_3O-), 2.41 (3H, s, CH_3-6), 1.99 (3H, s, CH_3-3); ^{13}C NMR (126 MHz, CD_3OD) δ: 6.6 (CH_3-3), 22.9 (CH_3-6), 50.6 (CH_3O-), 103.5 (C-1), 108.5 (C-3), 110.2 (C-5), 139.5 (C-6), 160.3 (C-2), 162.8 (C-4), 172.6 (C=O); The NMR data was in accordance with those reported in the literature[12], hence compound **8** was identified as methyl-β-orsellinate.

Compound 9 Colorless oil (MeOH), $C_{20}H_{18}O_6$, ESI-MS(positive): *m/z* 377 $[M+Na]^+$, ESI-MS (negative): *m/z* 353 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 6.71 (1H, brd, J = 8.1 Hz, H-5′), 6.68 (1H, d, J = 8.3 Hz, H-5), 6.61 (2H, s, H-2, 2′), 6.52 (2H, m, H-6, 6′), 5.90 (4H, td, J = 5.2, 1.2 Hz, -O-CH_2-O-), 4.16 (1H, dd, J = 9.0, 7.5 Hz, Ha-9′), 3.93 (1H, dd, J = 9.1, 7.7 Hz, H_b-9′), 2.91 (1H, dd, J = 13.7, 5.2 Hz, H_a-7), 2.79 (1H, dd, J = 13.7, 5.2 Hz, H_b-7), 2.64 (1H, m, H-8), 2.54 (1H, d, J = 2.7 Hz, H_a-7′), 2.52 (1H, s, H-8′), 2.49 (1H, m, H_b-7′); ^{13}C NMR (126 MHz, CD_3OD) δ: 34.2 (C-7), 37.6 (C-7′), 41.2 (C-8′), 46.3 (C-8), 71.4 (C-9′), 100.8 (-O-CH_2-O-), 100.9 (-O-CH_2-O-), 107.6 (C-5′), 107.7 (C-5), 108.5 (C-2′), 109.0 (C-2), 121.3 (C-6), 122.1 (C-6′), 131.6 (C-1′), 132.2 (C-1), 146.3 (C-4), 146.4 (C-4′), 147.8 (C-3), 147.8 (C-3′), 179.9 (C-9). The NMR data was in accordance with those reported in the literature[13], hence compound **9** was identified as hinokinin.

Compound 10 White amorphous powder (MeOH), $C_{18}H_{18}O_2$, ESI-MS(positive): *m/z* 289 $[M+Na]^+$, ESI-MS (negative): *m/z* 265 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 7.22 (1H, d, J = 1.9 Hz, H-2), 7.20 (1H, dd, J = 8.2, 2.2 Hz, H-6), 6.98 (1H, d, J = 2.1 Hz, H-2′), 6.90 (1H, dd, J = 8.2, 2.2 Hz, H-6′), 6.78 (2H, m, H-5, 3′), 5.91 ~ 6.06 (2H, m, H-8, 8′), 4.98 ~ 5.08 (4H, m, H-9, 9′), 3.38 (2H, d, J = 6.6 Hz, H-7, 7′); ^{13}C NMR (126 MHz, CD_3OD) δ: 33.9 (C-7′), 39.1 (C-7), 113.9 (C-5), 114.0 (C-5′), 114.1 (C-9), 115.4 (C-9′), 125.9 (C-6), 127.3 (C-6′), 127.7 (C-1′), 128.6 (C-3′), 130.1 (C-2), 130.5 (C-2′), 131.1 (C-1), 137.1 (C-8′), 138.2 (C-8), 151.9 (C-4), 153.8 (C-4′); The NMR data was in accordance with those reported in the literature[14], hence compound **10** was identified as magnolol.

Compound 11 Colorless crystal (MeOH), $C_7H_6O_4$, ESI-MS(positive): *m/z* 177 $[M+Na]^+$, ESI-MS (negative): *m/z* 153 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 7.45 (1H, d, J = 1.9 Hz, H-2), 7.43 (1H, dd, J = 8.2, 1.9 Hz, H-6), 6.81 (1H, d, J = 8.2 Hz, H-5); ^{13}C NMR (126 MHz, CD_3OD) δ: 114.6 (C-5), 116.6 (C-2), 122.1 (C-6), 122.7 (C-1), 144.6 (C-3), 150.1 (C-4), 169.0 (C=O), The NMR data was in accordance with those reported in the literature[15], hence compond **11** was identified as protocatechuic acid.

Compound 12 Colorless oil (MeOH), $C_{27}H_{26}O_3$, ESI-MS(positive): *m/z* 421 $[M+Na]^+$, ESI-MS (negative): *m/z* 397 $[M-H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.30 (1H, brs, H-3″), 7.26 (2H, d, J = 8.2 Hz, H-2′, 6′), 7.15 (2H, d, J = 8.2 Hz, H-3′, 5′), 7.03 (1H, d, J = 8.2 Hz, H-5″), 6.85 (1H, d, J = 8.2 Hz, H-6″), 5.99 (3H, m, H-8, 8′, 8″), 5.12 ~ 5.00 (6H, m, H-9, 9′, 9″), 3.36 (6H, d, J = 6.5

Hz, H-7, 7′, 7″); ^{13}C NMR (101 MHz, CD_3OD) δ: 40.4 (C-7′, 7″), 40.5 (C-7), 115.6 (C-9′, 9″), 115.8 (C-9), 117.0 (C-3), 117.1 (C-6″), 121.6 (C-2′,6′), 125.1 (C-6), 125.4 (C-5), 127.6 (C-2″), 129.1 (C-3′,5′), 129.9 (C-3″), 132.1 (C-3″), 132.9 (C-4′,4″), 133.7 (C-4), 139.3 (C-8), 139.5 (C-8′,8″), 141.5 (C-1), 147.8 (C-2), 152.4 (C-1″), 154.0 (C-1′). The NMR data was in accordance with those reported in the literature[6], hence copound **12** was identified as isodunnianol.

Compound 13 Yellow oil (MeOH), $C_{30}H_{34}O_9$, ESI-MS (positive): *m/z* 561 $[M+Na]^+$, ESI-MS (negative): *m/z* 537 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 6.93 (1H, brs, H-2), 6.93 (1H, brs, H-2′), 6.92 (1H, brs, H-6″), 6.81 (1H, dd, *J* = 8.2, 1.7 Hz, H-6), 6.76 (1H, d, *J* = 8.1 Hz, H-5), 6.73 (2H, brs, H-2″,6′), 5.52 (2H, d, *J* = 6.2 Hz, H-7, 7′), 3.85 (3H, s, CH_3O-3′), 3.83 (3H, s, CH_3O-3), 3.81 (3H, s, CH_3O-3″), 3.76 (2H, m, H-9), 3.59 ~ 3.55 (2H, m, H-9″), 3.51 (2H, m, H-9′), 2.62 (2H, *J* = 7.7 Hz, H-7″), 1.82 (2H, m, H-8″); ^{13}C NMR (126 MHz, CD_3OD) δ: 31.5 (C-8″), 34.4 (C-7″), 53.8 (C-8), 54.1 (C-8′), 54.97 (CH_3O-3), 55.34 (CH_3O-3″), 55.37 (CH_3O-3′), 60.82 (C-9″), 63.35 (C-9), 63.6 (C-9′), 87.9 (C-7), 87.8 (C-7′), 109.2 (C-2), 110.4 (C-2′), 112.7 (C-2″), 114.4 (C-5), 114.8 (C-6′), 116.5 (C-6″), 118.3 (C-6), 128.4 (C-5″), 128.9 (C-5′), 132.9 (C-1), 135.4 (C-1′), 135.6 (C-1″), 143.8 (C-3′), 144.0 (C-3″), 146.0 (C-4), 146.4 (C-4″), 147.8 (C-3), 147.8 (C-4). The NMR data was in accordance with those reported in the literature[16], hence compound **13** was identified as vitrifol A.

Compound 14 White amorphous powder (MeOH), $C_{20}H_{24}O_6$, ESI-MS (positive): *m/z* 383 $[M+Na]^+$, ESI-MS (negative): *m/z* 359 $[M-H]^-$; ^{1}H NMR (400Hz CD_3OD) δ: 6.95 (1H, brs, H-2′), 6.82 (d, *J* = 8.2 Hz, H-6′), 6.76 (1H, d, *J* = 8.2 Hz, H-5′), 6.71 (2H, brs, H-2,6), 5.48 (1H, d, *J* = 6.3 Hz, H-7′), 3.85 (3H, s, CH_3O-3), 3.79 (3H, s, CH_3O-3′), 3.75 (2H, m, H-9′), 3.56 (2H, t, *J* = 6.4 Hz, H-9), 3.47 (1H, m, H-8′), 2.61 (2H, t, *J* = 7.6 Hz, H-7), 1.81 (2H, m, H-8); ^{13}C NMR (101 MHz, CD_3OD) δ: 33.0 (C-7), 35.8 (C-8), 55.4 (C-8′), 56.4 (CH_3O-3), 56.8 (CH_3O-3′), 62.3 (C-9), 65.0 (C-9′), 89.0 (C-7′), 110.6 (C-2′), 114.1 (C-2), 116.2 (C-5′), 118.1 (C-6), 119.8 (C-6′), 130.1 (C-5), 134.81 (C-1′), 137.1 (C-1), 145.2 (C-3), 147.5 (C-4), 147.5 (C-4′), 149.1 (C-3′). The NMR data was in accordance with those reported in the literature[17], hence compound **14** was identified as (+)-dihydrodehydrodiconiferyl alcohol.

Compound 15 Colorless crystal (MeOH), $C_{20}H_{24}O_8$, ESI-MS (positive): *m/z* 415 $[M+Na]^+$, ESI-MS (negative): *m/z* 391 $[M-H]^-$; ^{1}H NMR (500 MHz, CD_3OD) δ: 7.02 (1H, d, *J* = 1.7 Hz, H-2), 6.94 (1H, d, *J* = 2.1 Hz, H-2′), 6.79 (1H, dd, *J* = 8.2, 1.8 Hz, H-6), 6.76 (1H, m, H-6′), 6.74 (2H, m, H-5,5′), 5.00 (1H, s, H-7), 3.87 (1H, d, *J* = 9.0 Hz, H_b-9), 3.85 (3H, s, CH_3O-3), 3.84 (3H, s, CH_3O-3′), 3.80 (1H, d, *J* = 11.5 Hz, H_a-9), 3.69 (1H, d, *J* = 11.5 Hz, H_a-9′), 3.68 (1H, d, *J* = 8.9 Hz, H_b-9′), 2.97 (1H, d, *J* = 13.9 Hz, H_a-7′), 2.90 (1H, d, *J* = 13.9 Hz, H_b-7′); ^{13}C NMR (126 MHz, CD_3OD) δ: 38.7 (C-7′), 55.0 × 2 (CH_3O-3, 3′), 63.0 (C-9), 73.4 (C-9′), 80.7 (C-8′), 81.0 (C-8), 84.8 (C-7), 111.5 (C-2), 114.0 (C-2′), 114.0 (C-5), 114.3 (C-5′), 120.3 (C-6), 122.7 (C-6′), 128.8 (C-1), 129.8 (C-1′), 144.7 (C-4), 145.7 (C-4′), 147.1 (C-3), 147.2 (C-3′). The NMR data was in accordance with those reported in the literature[18], hence compond **15** was identified as (-)-massoniresinol.

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