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CHEMICAL CONSTITUENTS OF *Combretum punctatum* spp. *squamosum*

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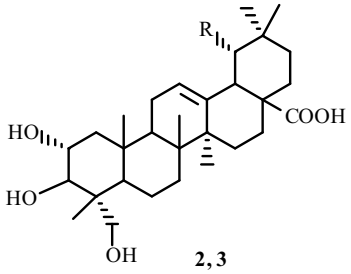
The plants of *Combretum* (Combretatace) are widely used in folk medicine for the treatment of leprosy, cancer, hepatitis, diarrhea, and respiratory infections in different parts of Asia and Africa. Some types of compounds such as stilbenes, phenanthrenes, triterpenes, and their glycosides were isolated from *Combretum* species, and these compounds showed various activities [1]. Eleven species are widespread in China, and most of them are distributed in Yunnan and Hainan Province [2]. Some species were used for the treatment of bruises, abdominal pain, diarrhea, jaundice, hepatitis, and ascariasis in Chinese folk medicine [3, 4]. It is necessary to investigate the chemical constituents of *Combretum* species from China. As part of our work, ten compounds were isolated from *Combretum punctatum* spp. *squamosum*. Their structures were determined by spectroscopic analysis to be oleanolic acid (**1**), arjunolic acid (**2**) [5], arjungenin (**3**) [6], quadranoside I (**4**) [7], vitexin (**5**) [8], methyl gallate (**6**) [9], stigmasta-4,25(26)dien-3-one (**7**) [10], octadecanoic acid (**8**), β-sitosterol (**9**), and β-daucosterol (**10**). This is the first time all the compounds were isolated from this plant.

The NMR spectra were recorded on Bruker AV-400 and Bruker DRX-500 spectrometers in deuterated reagent solution with TMS as an internal standard. The multiplicity of ^{13}C NMR, determined as DEPT MS data, were obtained on a VG Autospec-3000 spectrometer.

The materials were collected in September 2006 from Xishuangbanna in Yunnan province in China and identified by Wen Bin in Xishuangbanna Botanical Garden, Chinese Academy of Sciences.

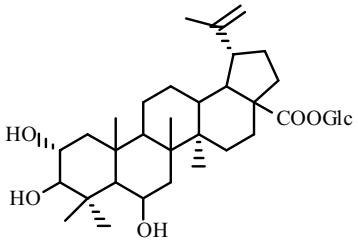
Extraction and Isolation. The air-dried and powdered leaves and stems of *Combretum punctatum* spp. *squamosum* (5 kg) were extracted with EtOH (3 ×) to give a crude extract. After concentration of the combined extracts, the resulting gummy material was suspended in water and then partitioned with ethyl acetate to afford ethyl acetate residues (65 g). The ethyl acetate residues (65 g) were subjected to CC over silica gel and eluted with petroleum ether–$CH_3COOCH_2CH_3$ (from 10:1 to 0:1) to give eight fractions. Each fraction was repeatedly subjected to CC over silica gel and Sephadex LH-20 to afford compound **7** and β-sitosterol from the second fraction, compounds **1** and **8** from the fifth fraction, and compounds **2–6** and β-daucosterol from the eighth fraction.

Oleanolic acid (1), colorless powder. ^{13}C NMR (100 MHz, CD_3OD, δ): 38.2 (t, C-1), 27.0 (t, C-2), 78.5 (d, C-3), 38.2 (s, C-4), 55.0 (d, C-5), 18.0 (t, C-6), 32.7 (t, C-7), 41.0 (s, C-8), 47.4 (d, C-9), 36.3 (s, C-10), 23.9 (t, C-11), 122.0 (d, C-12), 143.6 (s, C-13), 38.7 (s, C-14), 27.5 (t, C-15), 23.2 (t, C-16), 46.1 (s, C-17), 47.9 (d, C-18), 38.3 (t, C-19), 38.9 (s, C-20), 30.0 (t, C-21), 33.4 (t, C-22), 28.8 (q, C-23), 15.2 (q, C-24), 16.0 (q, C-25), 18.0 (q, C-26), 23.9 (q, C-27), 180.5 (s, C-28), 16.8 (q, C-29), 23.1 (q, C-30).



2, 3

2: R = H
3: R = OH



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Arjunolic acid (2), colorless needles. ^{13}C NMR (100 MHz, CD_3OD, δ): 47.5 (t, C-1), 69.6 (d, C-2), 78.0 (d, C-3), 40.2 (s, C-4), 48.3 (d, C-5), 19.5 (t, C-6), 33.2 (t, C-7), 33.0 (s, C-8), 48.1 (d, C-9), 38.9 (s, C-10), 23.9 (t, C-11), 123.4 (d, C-12), 145.3 (s, C-13), 42.7 (s, C-14), 30.5 (t, C-15), 24.2 (t, C-16), 44.1 (s, C-17), 42.9 (d, C-18), 47.3 (t, C-19), 38.9 (s, C-20), 34.0 (t, C-21), 33.4 (t, C-22), 66.1 (t, C-23), 13.8 (q, C-24), 17.5 (q, C-25), 17.7 (q, C-26), 26.4 (q, C-27), 181.8 (s, C-28), 33.6 (q, C-29), 23.9 (q, C-30).

Arjungenin (3), colorless powder. ^{13}C NMR (100 MHz, CD_3OD, δ): 47.5 (t, C-1), 69.5 (d, C-2), 74.0 (d, C-3), 40.2 (s, C-4), 47.9 (d, C-5), 19.6 (t, C-6), 33.2 (t, C-7), 33.6 (s, C-8), 48.5 (d, C-9), 38.7 (s, C-10), 24.0 (t, C-11), 123.4 (d, C-12), 145.3 (s, C-13), 42.7 (s, C-14), 31.6 (t, C-15), 24.4 (t, C-16), 42.7 (s, C-17), 42.5 (d, C-18), 84.5 (d, C-19), 38.9 (s, C-20), 34.9 (t, C-21), 33.8 (t, C-22), 67.5 (t, C-23), 12.7 (q, C-24), 16.3 (q, C-25), 17.8 (q, C-26), 27.4 (q, C-27), 181.8 (s, C-28), 33.6 (q, C-29), 23.9 (q, C-30).

Quadranoside I (4), colorless powder. ^{13}C NMR (100 MHz, CD_3OD, δ): 49.6 (t, C-1), 69.8 (d, C-2), 84.6 (d, C-3), 41.1 (s, C-4), 57.8 (d, C-5), 68.8 (d, C-6), 43.3 (t, C-7), 43.7 (s, C-8), 50.6 (d, C-9), 38.4 (s, C-10), 22.5 (t, C-11), 27.2 (t, C-12), 38.4 (d, C-13), 39.1 (s, C-14), 30.6 (t, C-15), 32.9 (t, C-16), 57.1 (s, C-17), 50.4 (d, C-18), 48.5 (d, C-19), 151.8 (s, C-20), 31.2 (t, C-21), 37.6 (t, C-22), 28.5 (q, C-23), 19.4 (q, C-24), 19.5 (q, C-25), 17.2 (q, C-26), 15.3 (q, C-27), 176.1 (s, C-28), 110.3 (t, C-29), 18.6 (q, C-30), 95.2 (d, C-1′), 71.0 (d, C-2′), 78.7 (d, C-3′), 74.0 (d, C-4′), 78.3 (d, C-5′), 62.3 (t, C-6′).

Vitexin (5), yellow solid. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 8.02 (2H, d, J = 8.8, H-2′, 6′), 6.92 (2H, d, J = 8.8, H-3′, 5′), 6.80 (s, H-3), 6.26 (s, H-6). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 163.9 (s, C-2), 102.5 (d, C-3), 182.1 (s, C-4), 156.0 (s, C-5), 98.1 (d, C-6), 162.6 (s, C-7), 104.0 (s, C-8), 161.9 (s, C-9), 104.6 (s, C-10), 129.0 (d, C-2′, 6′), 115.8 (d, C-3′, 5′), 121.6 (s, C-1′), 160.4 (s, C-4′), 73.4 (d, C-1″), 70.8 (d, C-2″), 78.6 (d, C-3″), 70.5 (d, C-4″), 81.9 (d, C-5″), 61.3 (t, C-6″); ESI-MS *m/z* 431 $[M - H]^+$.

Methyl gallate (6), colorless needles, $C_8H_8O_5$. ^1H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.02 (2H, s, J = 7.5, H-2,6), 3.80 (3H, s, OCH_3). ^{13}C NMR (100 MHz, CD_3OD, δ): 121.4 (s, C-1), 110.0 (d, C-2, 6), 146.5 (C-3, 5), 139.7 (s, C-4), 169.0 (C-7), 52.3 (q, OCH_3); EI-MS *m/z* (%): 184 (56), 153 (100), 125 (36), 112 (15), 107 (10), 79 (13).

Stigmasta-4,25(26)dien-3-one (7), colorless powder. ^{13}C NMR (125 MHz, $CDCl_3$, δ): 199.9 (s, C-3), 171.9 (s, C-5), 147.9 (s, C-25), 124.1 (d, C-4), 111.7 (t, C-26), 56.4 (d, C-17), 56.3 (d, C-14), 54.2 (d, C-9), 49.9 (d, C-24), 42.8 (s, C-13), 40.0 (t, C-12), 39.0 (s, C-10), 36.1 (d, C-20), 36.5 (t, C-1), 36.0 (d, C-8), 34.3 (t, C-22), 34.0 (t, C-2), 33.3 (t, C-6), 32.4 (t, C-7), 30.0 (t, C-23), 28.5 (t, C-16), 26.9 (t, C-28), 24.5 (t, C-15), 21.5 (t, C-11), 18.9 (q, C-21), 18.2 (q, C-27), 17.8 (q, C-19), 12.4 (q, C-29), 12.3 (q, C-18).

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