# FLAVONOIDS AND XANTHONES FROM *Tripterospermum chinense*

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*Tripterospermum chinense* (Migo) H. Smith (Gentianaceae), widely distributed in the southeast of China, is traditionally used for the treatment of coughs, haemoptysis, and pulmonary disease by local inhabitants [1]. In continuation of our research on bioactive compounds, seven flavonoids and two xanthones were isolated from the aerial parts of *T. chinense*.

Dried and chipped aerial parts (800 g) of *T. chinense* was extracted with boiled aqueous ethanol (95%). The solvent was evaporated in vacuum and then the concentrated extract was successively partitioned with ethyl acetate and *n*-butanol. The ethyl acetate fraction was successively purified on silica gel with $CHCl_3$–MeOH gradient and on ODS with MeOH–$H_2O$ to yield compounds **1–7**. The *n*-butanol extract was purified using silica gel with $CHCl_3$–MeOH gradient as eluent to give compounds **8** and **9**.

**Methyllanceolin (1)**: yellow crystal (methanol), $C_{16}H_{14}O_7$, mp 215–217°C, ESIMS *m/z* 341 $[M+Na]^+$.

PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.74 (3H, s, OMe), 3.77 (3H, s, OMe), 3.90 (3H, s, OMe), 6.47 (1H, s, H-2), 7.22 (1H, d, J = 9.1, H-5), 7.37 (1H, d, J = 9.1, H-6).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 180.2 (C-9), 159.3 (C-1), 158.2 (C-3), 149.4 (C-4b), 145.5 (C-4a), 145.3 (C-8), 137.5 (C-7), 127.5 (C-4), 124.3 (C-6), 113.5 (C-8a), 113.4 (C-5), 102.9 (C-8b), 94.8 (C-2), 61.0, 60.7, 56.5 (OMe) [2].

**(+)-Catechin (2)**: white powder, $C_{15}H_{14}O_6$, mp 238–240°C, ESIMS *m/z* 313 $[M+Na]^+$ and (–)-epicatechin (**3**): white powder, $C_{15}H_{14}O_6$, mp 173–174°C, ESIMS *m/z* 313 $[M+Na]^+$.

$^1$H NMR and $^{13}$C NMR data were in good agreement with those reported for **2** and **3** in the literature [3, 10].

PMR (400 MHz, $CD_3OD$, δ, ppm, J/Hz): 2.73 (1H, dd, J = 12.8, 2.9, H-4a), 2.87 (1H, dd, J = 12.8, 4.6, H-4b), 4.19 (1H, m, H-3), 4.82 (1H, br.s, H-2), 5.94 (1H, d, J = 2.3, H-6), 5.97 (1H, d, J = 2.3, H-8), 6.82 (1H, d, J = 8.4, H-5′), 6.76 (1H, dd, J = 8.4, 1.9, H-6′), 6.98 (1H, d, J = 1.9, H-2′).

$^{13}$C NMR (100 MHz, $CD_3OD$, δ, ppm): 158.0 (C-7), 157.7 (C-5), 157.4 (C-9), 146.0 (C-4′), 145.8 (C-3′), 132.3 (C-1′), 119.4 (C-6′), 115.9 (C-5′), 115.3 (C-2′), 100.1 (C-10), 96.4 (C-6), 95.9 (C-8), 79.9 (C-2), 67.5 (C-3), 29.3 (C-4) [3].

**Kaempferol-7-*O*-β-D-glucopyranoside (4)**: yellow crystal (methanol), $C_{21}H_{20}O_{11}$, mp 270–271°C, ESIMS *m/z* 471 $[M+Na]^+$.

PMR (400 MHz, $CD_3OD$, δ, ppm, J/Hz): 3.25–4.23, (6H, m, H-2″-6″), 5.11 (1H, d, J = 7.0, H-1″), 6.26 (1H, d, J = 1.8, H-6), 6.46 (1H, d, J = 1.8, H-8), 6.90 (2H, d, J = 8.2, H-3′, 5′), 8.12 (2H, d, J = 8.2, H-2′, 6′).

$^{13}$C NMR (100 MHz, $CD_3OD$, δ, ppm): 179.9 (C-4), 167.0 (C-7), 162.5 (C-5), 162.1 (C-4′), 159.3 (C-9), 158.6 (C-2), 133.6 (C-3), 132.6 (C-2′, 6′), 123.1 (C-1′), 116.3 (C-3′, 5′), 106.1 (C-10), 105.1 (C-1″), 100.9 (C-6), 95.2 (C-8), 77.2 (C-5″), 75.1 (C-3″), 73.1 (C-2″), 70.3 (C-4″), 61.9 (C-6″) [4].

**Isovitexin (5)**: yellow crystal (methanol), $C_{21}H_{20}O_{10}$, mp 210–212°C, ESIMS *m/z* 455 $[M+Na]^+$.

PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.31–4.35, (6H, m, H-2″-6″), 4.57 (1H, d, J = 9.9, H-1″), 6.45 (1H, s, H-8), 6.71 (1H, s, H-3), 6.91 (2H, d, J = 8.2, H-3′, 5′), 7.92 (2H, d, J = 8.2, H-2′, 6′).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 181.9 (C-4), 163.9 (C-7), 163.0 (C-2), 162.1 (C-4′), 160.0 (C-5), 157.3 (C-9), 128.6 (C-2′, 6′), 121.1 (C-1′), 116.5 (C-3′, 5′), 108.9 (C-6), 103.1 (C-10), 102.6 (C-3), 94.2 (C-8), 81.2 (C-5″), 79.1 (C-3″), 73.2 (C-1″), 70.6 (C-2″), 70.3 (C-4″), 61.4 (C-6″) [5].

**Isoorientin (6)**: yellow powder, $C_{21}H_{20}O_{11}$, mp 227–229°C, ESIMS *m/z* 471 $[M+Na]^+$.

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PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.29–4.34, (6H, m, H-2″-6″), 4.62 (1H, d, J = 9.7, H-1″), 6.52 (1H, s, H-8), 6.83 (1H, s, H-3), 6.89 (1H, d, J = 8.6, H-5′), 7.49 (1H, d, J = 1.9, H-2′), 7.52 (1H, dd, J = 8.6, 1.9, H-6′).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 181.6 (C-4), 164.2 (C-2), 163.6 (C-7), 160.9 (C-5), 157.2 (C-9), 149.8 (C-4′), 146.2 (C-3′), 121.7 (C-1′), 118.9 (C-6′), 116.0 (C-5′), 113.7 (C-2′), 108.8 (C-6), 103.2 (C-10), 102.4 (C-3), 94.0 (C-8), 81.3 (C-5″), 79.0 (C-3″), 73.2 (C-1″), 70.5 (C-2″), 70.1 (C-4″), 61.2 (C-6″) [5].

**Kaempferol-3-*O*-α-L-rhamnopyranoside (7)**: yellow powder, $C_{21}H_{20}O_{10}$, mp 174–175°C, ESIMS *m*/*z* 455 $[M+Na]^+$.

PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 0.90 (3H, d, J = 5.9, H-6″), 3.30–4.22 (4H, m, H-2″-5″), 5.29 (1H, d, J = 1.8, H-1″), 6.24 (1H, d, J = 2.0, H-6), 6.45 (1H, d, J = 2.0, H-8), 6.91 (2H, d, J = 8.7, H-3′, 5′), 7.80 (2H, d, J = 8.7, H-2′, 6′).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 178.4 (C-4), 166.5 (C-7), 162.9 (C-5), 161.0 (C-4′), 159.4 (C-2), 158.3 (C-9), 135.4 (C-3), 132.0 (C-2′, 6′), 122.7 (C-1′), 115.9 (C-3′, 5′), 105.1 (C-10), 103.6 (C-1″), 100.5 (C-6), 95.3 (C-8), 73.4 (C-4″), 72.3 (C-2″), 72.1 (C-3″), 71.9 (C-5″), 18.2 (C-6″) [6, 7].

**Triptexanthoside D (8)**: yellow powder, $C_{26}H_{30}O_{16}$, mp 240–241°C, ESIMS *m*/*z* 621 $[M+Na]^+$.

PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.51–4.18 (12H, m, H-2′-6′, H-2″-5″), 3.77 (3H, s, OMe-5), 3.95 (3H, s, OMe-6), 4.16 (1H, d, J = 7.2, H-1″), 4.89 (1H, d, J = 7.9, H-1′), 6.58 (1H, s, H-7), 7.02 (1H, d, J = 9.0, H-4), 7.72 (1H, d, J = 9.0, H-3).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 184.1 (C-9), 160.5 (C-6), 157.6 (C-8), 150.0 (C-4b), 149.2 (C-4a), 148.9 (C-1), 140.3 (C-2), 128.2 (C-5), 125.4 (C-3), 107.3 (C-8b), 106.2 (C-4), 103.5 (C-1″), 101.3 (C-8a), 101.0 (C-1′), 95.1 (C-7), 76.7 (C-3′), 76.5 (C-3″), 76.0 (C-5′), 73.5 (C-2′), 73.2 (C-2″), 69.7 (C-4′), 69.4 (C-4″), 68.2 (C-6′), 65.6 (C-5″), 60.7 (5-OMe), 56.5 (6-OMe) [8].

**Lisovitexin-2-*O*-α-L-rhamnopyranoside (9)**: yellow powder, $C_{27}H_{30}O_{14}$, mp 218–220°C, ESIMS *m*/*z* 601 $[M+Na]^+$.

PMR (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 0.75 (3H, d, J = 6.2, H-6‴), 2.57–4.25 (11H, m, H-2″-6″, H-2‴-5‴), 4.75 (1H, d, J = 9.6, H-1″), 5.06 (1H, d, J = 1.8, H-1‴), 6.49 (1H, s, H-3), 6.68 (1H, s, H-8), 6.93 (2H, d, J = 8.9, H-3′, 5′), 7.90 (2H, d, J = 8.9, H-2′, 6′).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, δ, ppm): 181.9 (C-4), 163.9 (C-2), 163.0 (C-7), 161.1 (C-4′), 161.0 (C-5), 157.3 (C-9), 128.5 (C-2′, 6′), 121.1 (C-1′), 115.9 (C-3′, 5′), 108.9 (C-6), 103.5 (C-10), 102.6 (C-3), 100.7 (C-1‴), 94.2 (C-8), 81.2 (C-5″), 79.6 (C-2″), 76.1 (C-3″), 72.1 (C-4‴), 71.9 (C-1″), 70.8 (C-4″), 70.6 (C-2‴, 3‴), 68.0 (C-5‴), 61.5 (C-6″), 17.3 (C-6‴) [9].

Thus, all these compounds were isolated from *T. chinense* for the first time. Compounds **5**, **6**, **8,** and **9** were isolated from another species *T. joponicum* [8, 9], compound **1** was isolated from *T. lanceolatum* [2], and other compounds were identified for the first time in the genus *Tripterospermum*.

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