Chemistry of Natural Compounds, Vol. 47, No. 3, July, 2011 [Russian original No. 3, May–June, 2011]

CHEMICAL CONSTITUENTS FROM THE ANTITUMOR FRACTION OF *Trachyrhamphus serratus*

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Trachyrhamphus serratus Temminck et Schlegel, a pipefish widely distributing in Western Pacific Ocean and Northern Indian Ocean, has been used for the treatment of impotence and tumor for more than 500 years in China [1, 2]. It was reported that the ethanol extract of *Trachyrhamphus serratus* showed obvious antitumor activity *in vivo* [3] and *in vitro* [4]. Moreover, the active components were confirmed in the petroleum ether soluble fraction of the ethanol extract according to active-guided screening in our preliminary studies [5]. In order to find the antitumor constituents, chemical separation was carried out on the petroleum ether fraction. As a result, 12 compounds were isolated and identified, including a new natural product **9**. Compounds **2–12** were obtained from *Trachyrhamphus serratus*, and compound **6** was found in the vertebrate for the first time.

The dried *Trachyrhamphus serratus* was obtained from Haikou, Hannan province of China, in November, 2005 and was authenticated by one of the authors, Prof. Xiaobo Li. The whole body of *Trachyrhamphus serratus* (517 g) was extracted with 95% alcohol by reflux for three times (2 h each time) and filtered. The ethanol extract (69.3 g) was partitioned with water and petroleum ether (30–60°C). The petroleum ether soluble fraction was evaporated to yield the petroleum ether extract (31.8 g). Part of the petroleum ether extract (26.4 g) was chromatographed on a silica gel column (mesh 200–300) and subjected to preparative TLC and preparative HPLC to afford compounds **1–12**.

Cholestanol (1). $C_{27}H_{46}O$, white needle, mp 147–149°C; EI-MS *m/z* 386 $[M]^+$; ^1H and ^{13}C NMR spectral data were consistent with those reported in the literature [6].

Oleic Acid (2). $C_{18}H_{34}O_2$, yellow oil; EI-MS *m/z* 282 $[M]^+$; ^1H NMR spectral data were consistent with those reported in the literature [7].

Cholesteryl Stearate (3). $C_{45}H_{80}O_2$, white needle, mp 80–81°C; EI-MS *m/z* 652 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [8].

Cholesteryl Myristate (4). $C_{41}H_{72}O_2$, white powder, mp 70–72°C; EI-MS *m/z* 596 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [9].

1-Triacontanol (5). $C_{30}H_{62}O$, white powder, mp 77–79°C; ESI-MS *m/z* 439.8 $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, J/Hz): 0.90 (3H, t, J = 6.6, H-30), 1.60 (2H, m, H-2), 3.68 (2H, t, J = 6.6, H-1). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 63.1 (C-1), 33.1 (C-2), 25.9 (C-3), 29.5–29.9 (C-4–C-27), 32.1 (C-28), 22.7 (C-29), 14.3 (C-30) [10].

24-Ethylcholesta-4,24(28)-dien-3-one (6). $C_{29}H_{46}O$, white needle, mp 86–87°C. EI-MS *m/z* 410 $[M]^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, J/Hz): 0.72 (3H, s, 18-CH_3), 0.98 (3H, d, J = 6.6, 21-CH_3), 1.00 (6H, dd, J = 6.7, 1.2, 26-CH_3 and 27-CH_3), 1.15 (3H, s, 19-CH_3), 1.59 (3H, d, J = 6.6, 29-CH_3), 5.20 (1H, q, J = 6.6, H-28), 5.75 (1H, s, H-4). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 35.8 (C-1), 34.1 (C-2), 199.0 (C-3), 123.4 (C-4), 171.4 (C-5), 33.0 (C-6), 32.3 (C-7), 35.6 (C-8), 53.9 (C-9), 38.8 (C-10), 21.2 (C-11), 39.7 (C-12), 42.5 (C-13), 66.0 (C-14), 24.3 (C-15), 28.3 (C-16), 56.0 (C-17), 12.0 (C-18), 17.5 (C-19), 36.5 (C-20), 18.8 (C-21), 35.3 (C-22), 25.8 (C-23), 147.1 (C-24), 34.9 (C-25), 22.2 (C-26), 22.4 (C-27), 115.8 (C-28), 13.3 (C-29) [11].

Cholest-4-en-3-one (7). $C_{27}H_{44}O$, white needle, mp 79–80°; EI-MS *m/z* 384 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [12].

Squalene (8). $C_{30}H_{50}$, colorless oil; EI-MS *m/z* 410 $[M]^+$; ^1H and ^{13}C NMR spectral data were consistent with those reported in the literature [13].

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0009-3130/11/4703-0465

Cholest-5-en-3β,7α-diol, 3-oleate (9). $C_{45}H_{78}O_3$, white needle, mp 44–46°C; EI-MS *m/z* 666 $[M]^+$. Alkaline hydrolysis yielded cholest-5-en-3β,7α-diol and compound **2**; IR (KBr, ν, cm^{-1}): 2960 (C=C), 1738 (C=O), 1636 (C=C), 1380 (CH_3), 1182 (C-O-C). ^1H NMR (400 MHz, $CDCl_3$, δ, J/Hz): 0.68 (3H, s, 18-CH_3), 0.92 (3H, d, J = 6.6, 21-CH_3), 1.15 (3H, s, 19-CH_3), 3.86 (1H, br.s, H-7), 4.62 (1H, m, H-3), 5.30 (2H, m, H-9′ and H-10′), 5.41 (1H, d, J = 4.4, H-6). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 37.2 (C-1), 29.4 (C-2), 74.6 (C-3), 40.1 (C-4), 146.2 (C-5), 122.1 (C-6), 68.0 (C-7), 35.6 (C-8), 42.3 (C-9), 37.7 (C-10), 21.0 (C-11), 39.4 (C-12), 42.4 (C-13), 49.5 (C-14), 24.4 (C-15), 28.4 (C-16), 56.1 (C-17), 11.8 (C-18), 18.6 (C-19), 36.0 (C-20), 19.0 (C-21), 36.4 (C-22), 24.0 (C-23), 39.8 (C-24), 28.2 (C-25), 22.8 (C-26), 23.0 (C-27), 173.4 (C-1′), 34.5 (C-2′), 24.6 (C-3′), 129.6 (C-9′), 129.8 (C-10′), 29.9–28.7 (C-4′–C-7′, C-12′–C-15′), 31.6 (C-16′), 22.5 (C-17′), 14.0 (C-18′) [14].

Cholest-5-en-3β-ol-7-one (10). $C_{27}H_{44}O_2$, white needle, mp 165–167°C; EI-MS *m/z* 400 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [15].

Hexadecanoic Acid, 2,3-Dihydroxypropyl Ester (11). $C_{19}H_{38}O_4$, white needle, mp 68–69°C; EI-MS *m/z* 330 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [16].

Cholest-4-en-6β-ol-3-one (12). $C_{27}H_{44}O_2$, white needle, mp 175–177°C; EI-MS *m/z* 400 $[M]^+$. ^1H and ^{13}C NMR spectral data agreed with those reported in [17].

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No. 30672620) and the Shanghai Scientific Committee – Korea SK Research & Development Foundation (No.200312t).

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