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CHEMICAL CONSTITUENTS FROM PINE NEEDLES OF *Cedrus deodara*

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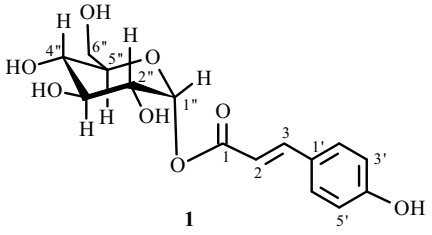
The plant *Cedrus deodara* (Roxb.) Loud. belonging to the *Pinus* (Pinaceae) is an evergreen tree growing extensively on the slopes of the Himalayas. The wood of *Cedrus deodara* has been used since ancient days in Indian medical practice for the treatment of inflammations and rheumatoid arthritis. It is recorded in the dictionary of Chinese Crude Drugs as an effective herbal drug for expelling wind, removing dampness, destroying parasites, and relieving itching. Its indications are wind-cold-dampness arthralgia, traumatic injury, sleeplessness, edema, eczema, and acariasis. In recent years, pine needles are used for rheumatism, cardiovascular diseases, diabetes, obesity, liver and stomach diseases, gonorrhea, chronic bronchitis, cancer, etc. [1]. No phytochemical work on the needles of this genus has so far been reported. The medicinal importance of *Cedrus deodara* prompted us to carry out phytochemical investigations on this genus.

In the present work, we isolated and elucidated the structure of one new phenylpropanoid **1** along with nine known compounds **2–10**, all of which were obtained from this plant for the first time.

The pine needles of *Cedrus deodara* were collected from Lanzhou City of Gansu province of China in June 2008.The plant sample was identified by Prof. Fu Jiang He at Gansu Academy of Medical Science. The air-dried pine needles of *Cedrus deodara* (3.5 kg) were extracted with 95% ethanol (10 times volume) three times to afford an ethanol extract (390 g) that was suspended in water, and extracted with petroleum ether, ethyl acetate, and *n*-butanol, separately. The petroleum ether residue (51 g) was chromatographed on a silica gel column gradiently eluted with petroleum ether–ethyl acetate (9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 v/v) to yield compounds **2** (65 mg), **4** (26 mg), **5** (31 mg), **6** (23 mg), and **7** (27 mg). The *n*-butanol extract (130 g) was chromatographed over Diaion HP-20 with H_2O containing increasing amounts of MeOH. The 20% MeOH eluate (3.4 g) was chromatographed on Toyopearl HW-40 (coarse grade) developing with 20% MeOH–50% MeOH. The 30% MeOH eluate (1.8 g) was rechromatographed on silica gel and Sephadex LH-20 to yield compound **1** (35 mg), **3** (35 mg), **8** (21 mg), **9** (26 mg), and **10** (37.7 mg).

The structures of these compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and MS. Besides compound **1**, the data of other compounds were in good agreement with the respective literature data.

The ESI-MS of compound **1** gave an $[M - H]^-$ ion at *m/z* 325, which indicated that the molecular formula of compound **1** was $C_{15}H_{18}O_8$. The characteristic signals for 1,4-disubstituted benzene protons at δ 7.556 (2H, d, J = 7.6 Hz) and 7.124 (2H, d, J = 7.6 Hz) and the pair of *trans*-olefinic proton signals at δ 7.642 (1H, d, J = 16.0 Hz) and 6.381 (1H, d, J = 16.0 Hz), which were conjugated with a carbonyl group, clearly indicated that there is a *trans*-coumaroyl moiety in the structure. The anomeric proton signal at δ 4.996 (1H, d, J = 4.4 Hz) of the sugar unit demonstrated α-D-configuration. Therefore, compound **1** was identified as 1-[3-(4-hydroxyphenyl)-2-propenoate]-α-D-glucopyranoside, which has not been reported previously.



1

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1-[3-(4-Hydroxyphenyl)-2-propenoate]-α-D-glucopyranoside (1). Colorless needle crystal, $C_{15}H_{18}O_8$. ESI-MS *m/z*: 325.0923 $[M - H]^-$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.300–3.460 (4H, m, H-2″, H-3″, H-4″, H-5″), 3.676 (1H, dd, J = 12.0, 4.0, H-6″a), 3.877 (1H, dd, J = 12.0, 2.0, H-6″b), 4.966 (1H, d, J = 4.4, H-1″), 6.381 (1H, d, J = 16.0, H-2), 7.124 (2H, d, J = 7.6, H-3′, 5′), 7.556 (2H, d, J = 7.6, H-2′, 6′), 7.642 (1H, d, J = 16.0, H-3). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 62.437 (C-6″), 71.273 (C-4″), 74.821 (C-2″), 77.926 (C-3″), 78.232 (C-5″), 101.825 (C-1″), 117.482 (C-2), 117.947 (C-3′, C-5′), 129.965 (C-1′), 130.736 (C-2′, C-6′), 145.874 (C-3), 160.814 (C-4′), 170.688 (C-1).

β-Sitosterol (2). Colorless needles, mp 136–138°C. EI-MS *m/z*, %: 414 ($[M]^+$, 10).

The spectral data agreed with those reported in the literature for β-sitosterol [2].

Shikimic Acid (3). $C_7H_{10}O_5$. Colorless needles, mp 189–190°C. ESI-MS *m/z*: 173.0455 $[M - H]^-$. IR (KBr, cm^{-1}): 3482, 2852–2520, 1681, 1647, 1276, 1076, 929, 862, 73. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm): 2.112 (1H, m, 6-H_b), 2.623 (1H, m, 6-H_a), 3.655 (1H, m, H-5), 3.972 (1H, m, H-4), 4.371 (1H, m, H-3), 6.791 (1H, m, H-2). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 31.626 (C-6), 67.320 (C-5), 68.411 (C-4), 72.707 (C-3), 130.705 (C-1), 138.847 (C-2), 170.040 (C=O) [3].

10-Nonacosanol (4). Colorless crystal, $C_{29}H_{60}O$. EI-MS *m/z* (%): 424 ($[M]^+$, 1), 407 ($[M - OH]^+$, 3), 406 ($[M - H_2O]^+$, 50), 297 ($[C_{19}H_{39}CH(OH)]^+$, 67), 157 ($[C_9H_{19}CH(OH)]^+$, 75), 97 (90), 83 (100). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.856 (6H, t, J = 7.2), 1.122–1.405 (54H, m), 3.560 (1H, br.s, CHOH). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.126 (2 × CH_3), 22.687 (2 × CH_2), 25.648 (CH_2), 29.700–29.326 (20 × CH_2), 31.920 (CH_2), 37.467 (2 × CH_2), 72.040 (CHOH) [4].

Dibutylphthalate (5). Yellow oil, $C_{16}H_{22}O_4$. ESI-MS *m/z*: 317 $[M + K]^+$, 301 $[M + Na]^+$, 279 $[M + 1]^+$, 221 $[M - C_4H_9]^+$, 205 $[M - C_4H_9O]^+$, 149 $[C_8H_4O_3]^+$. IR (KBr, cm^{-1}): 3437, 3071, 2961, 2876, 1727, 1600, 1581, 1488, 1470, 1394, 1375, 1304, 1287, 1137, 1123, 1074, 1040, 961, 927, 744. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.969 (6H, t, H-4′), 1.439 (4H, m, H-3′), 1.691 (4H, m, J = 6.8, H-2′), 4.271 (4H, m, J = 6.8, H-1′), 7.657 (2H, dd, J = 3.6, 5.6, H-4, 5), 7.756 (2H, dd, J = 3.6, 5.6, H-3, 6). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 13.534 (C-4′), 19.012 (C-3′), 31.770 (C-2′), 65.107 (C-1′), 128.820 (C-3, 6), 131.200 (C-4, 5), 131.246 (C-1, 2), 167.500 (COO) [5].

Protocatechuic Acid (6). Colorless needles, mp 199–200°C, $C_7H_6O_4$. EI-MS *m/z* (%): 154 ($[M]^+$, 78), 137 ($[M - OH]^+$, 100), 109 ($[M - COOH]^+$, 28). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.747 (1H, d, J = 8.0, H-5), 7.262 (1H, dd, J = 8.0, 2.0, H-6), 7.313 (1H, d, J = 2.0, H-2). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 115.208 (C-5), 116.856 (C-2), 121.678 (C-1), 122.960 (C-6), 144.935 (C-3), 149.849 (C-4), 168.078 (C-7) [6].

Phthalic Acid *bis*-(2-Ethylhexyl)ester (7). Yellow oil, $C_{24}H_{38}O_4$. EI-MS *m/z*: 391, 279, 167, 149. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.835–0.969 (12H, m, H-6′, 8′), 1.367–1.460 (16H, m, H-3′, 4′, 5′, 7′), 1.727 (2H, m, J = 6.8, H-2′), 4.296 (4H, m, J = 6.8, H-1′), 7.512 (2H, dd, J = 3.2, 5.2, H-4, 5), 7.700 (2H, dd, J = 3.2, 5.2, H-3, 6). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 10.921 (C-8′), 14.027 (C-6′), 22.947 (C-5′), 23.679 (C-7′), 28.876 (C-4′), 30.302 (C-3′), 38.665 (C-2′), 68.103 (C-1′), 128.802 (C-3, 6), 130.893 (C-4, 5), 132.389 (C-1, 2), 167.709 (COO) [7].

5-*p-trans*-Coumaroylquinic Acid (8). White powder, $C_{16}H_{18}O_8$. ESI-MS *m/z*: 339 $[M + H]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 1.921–2.226 (4H, m, H-2″, 6″), 3.739 (1H, dd, J = 9.6, 3.0, H-4″), 3.996 (1H, d, J = 4.4, H-3″), 5.33 (1H, m, H-5″), 6.352 (1H, d, J = 16.0, H-2), 6.807 (2H, d, J = 7.6, H-3′, 5′), 7.467 (2H, d, J = 8.0, H-2′, 6′), 7.659 (1H, d, J = 15.6, H-3). ^{13}CNMR (100 MHz, CD_3OD, δ, ppm): 37.251 (C-2″), 37.585 (C-6″), 71.258 (C-4″), 73.623 (C-3″), 76.469 (C-5″), 79.979 (C-1″), 115.346 (C-2), 116.811 (C-3′, 5′), 127.211 (C-1′), 131.178 (C-2′, 6′), 146.668 (C-3), 161.303 (C-4′), 168.872 (C-1), 176.480 (C-7″) [8].

Ferulic Acid β-D-Glucoside (9). White needle crystal, mp 184–186°C, $C_{16}H_{20}O_9$. ESI-MS *m/z*: 379 $[M + Na]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.296–3.339 (4H, m, H-2″, 3″, 4″, 5″), 3.339 (1H, dd, J = 4.1, 1.7, H-6_a″), 3.531 (1H, dd, J = 4.2, 3.3, H-6_b″), 3.693 (3H, s, 3-OCH_3), 4.955 (1H, d, J = 7.3, H-1″), 6.369 (1H, d, J = 15.6, H-2), 7.102 (1H, d, J = 8.3, H-5′), 7.091 (1H, dd, J = 8.3, 1.6, H-6′), 7.243 (1H, d, J = 1.6, H-2′), 7.591 (1H, d, J = 15.7, H-3). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 56.792 (3-OCH_3), 62.452 (C-6″), 71.265 (C-4″), 74.798 (C-2″), 77.850 (C-5″), 78.285 (C-3″), 101.847 (C-1″), 112.408 (C-2′), 115.796 (C-2), 117.963 (C-5′), 123.411 (C-6′), 129.973 (C-1′), 146.103 (C-3), 150.002 (C-4′), 151.017 (C-3′), 170.612 (C-1) [9].

(+)-(6*S*,9*R*)-9-*O*-β-D-Glucopyranosyloxy-6-hydroxy-3-oxo-α-ionol (10). Amorphous colorless powder, $C_{19}H_{30}O_8$. ESI-MS *m/z*: 409 $[M + Na]^+$, 795 $[2M + Na]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.901, 0.904 (each 3H, each s, H-11, 12), 1.161 (3H, d, J = 6.4, H-10), 1.786 (3H, d, J = 0.8, H-13), 2.041 (1H, d, J = 16.8, H-2a), 2.408 (1H, d, J = 16.8, H-2b), 2.972 (1H, ddd, J = 10.6, 8.4, 2.4, H-5′), 3.059 (1H, dd, J = 9.2, 6.0, H-2′), 3.101 (1H, t, J = 9.6, H-4′), 3.148 (1H, t, J = 9.6, H-3′), 3.428 (1H, dd, J = 11.2, 5.6, H-6a′), 3.649 (1H, dd, J = 11.6, 4.8, H-6b′), 4.161 (1H, d, J = 7.6, H-1′), 4.308 (1H, dq, J = 6.0, 5.6, H-9), 4.952 (1H, s, H-6-OH), 5.716 (1H, dd, J = 12.8, 6.4, H-8), 5.732 (1H, s, H-4), 5.848 (1H, d, J = 12.8, H-7).

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 19.074 (C-13), 21.042 (C-10), 23.146 (C-11), 24.209 (C-12), 41.072 (C-1), 48.847 (C-2), 61.269 (C-6′), 70.174 (C-4′), 73.813 (C-9), 74.988 (C-2′), 76.858 (C-3′), 76.934 (C-5′), 78.056 (C-6), 101.092 (C-1′), 125.821 (C-4), 130.484 (C-8), 133.536 (C-7), 164.286 (C-5), 197.653 (C-3) [10].

Phytochemical studies of the plant are continued.

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