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CHEMICAL CONSTITUENTS OF *Capparis spinosa*

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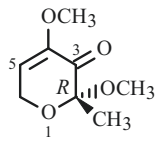
The stems and fruits of *Capparis spinosa* L. are used in Chinese traditional medicine for the treatment of arthritis, rheumatoid arthritis, etc. [1]. Biological studies have revealed that *Capparis* species has significant antidiabetic, antisclerotic, antimicrobial, antioxidative, anti-inflammatory, and antiviral activities, providing support for its ancient uses [2, 3]. In previous research, a number of substances of *Capparis* species have been isolated and studied by Chinese scientists [4–6]. In order to find new active compounds, we studied the isolation of compounds from *C. spinosa* L. Eleven compounds (**1–11**) were isolated from the methanol extract of the fruits of *C. spinosa* L. by silica gel, Sephadex LH-20, and RP-18 column chromatography. Their structures were determined by analysis of multiple spectra (LC-MS, ^{1}H NMR, ^{13}C NMR, and specific rotation). Compounds **1**, **2**, **4**, **9**, and **10** were isolated from the plant for the first time. The absolute configuration of compound **1** was determined by comparison of its experimental and calculated specific rotation. We report herein the isolation and structural identification of compounds from this species.

(*R*)-2,4-Dimethoxy-2-methyl-6*H*-pyran-3-one (1). A white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.51 (3H, s, 2-CH_3), 3.36 (3H, s, 2-OCH_3), 3.64 (3H, s, 4-OCH_3), 4.32 (1H, dd, J = 17.4, 4.5, H-6), 4.57 (1H, dd, J = 17.4, 2.0, H-6), 5.82 (1H, dd, J = 4.5, 2.0, H-5). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 186.4 (s, C-3), 146.6 (s, C-4), 113.0 (d, C-5), 99.6 (s, C-2), 59.4 (t, C-6), 54.9 (q, 4-OCH_3), 50.0 (q, 2-OCH_3), 17.7 (q, 2-CH_3). ESI-MS *m/z*: 195 $[M + Na]^+$, 367 $[2M + Na]^+$. The above data were consistent with the literature [5]. However, the chiral center of the compound was not determined in the above reference. In order to resolve the problem, the stereochemistry of the chiral center was assigned by comparison of its experimental and calculated specific rotation for the first time in our paper. The experimental specific rotation was $[\alpha]_D^{25}$–14.8° (*c* 0.14, MeOH) when we selected the *R* configuration to compute the specific rotation $[\alpha]_D^{25}$–17.0° at the level of B3LYP/6-311++G(2d, p)//B3LYP/6-311++G(2d, p) using quantum methods. This is very close to the experimental values, hence the absolute configuration of compound **1** was determined to be the *R* configuration.

Indole-3-carboxylic Acid (2). Brown crystals, mp 226–228°C. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm): 8.08 (1H, br.s, H-4), 7.94 (1H, s, H-2), 7.42 (1H, br.s, H-7), 7.17 (1H, br.s, H-6), 7.17 (1H, br.s, H-5). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 169.2 (s, COOH), 138.2 (s, C-8), 133.4 (d, C-2), 127.6 (s, C-9), 123.5 (d, C-6), 122.3 (d, C-5), 122.1 (d, C-4), 112.9 (d, C-7), 109.1 (s, C-3). ESI-MS *m/z* 184 $[M + Na]^+$. The above data were consistent with the literature [6].

1*H*-Indole-3-acetonitrile 4-*O*-α-Glucopyranoside (3). White solid. ^{1}H NMR (400 MHz, C_5D_5N, δ, ppm, J/Hz): 7.43 (1H, s, H-2), 7.34 (1H, d, J = 7.5, H-5), 7.24–7.13 (2H, overlap, H-6/7), 5.74–4.16 (9H, overlap). ^{13}C NMR (100 MHz, C_5D_5N, δ, ppm): 153.3 (s, C-4), 139.5 (s, C-7a), 123.6 (d, C-2), 123.3 (d, C-6), 120.6 (s, C-9), 118.3 (s, C-3a), 106.9 (d, C-7), 105.2 (s, C-3) , 105.0 (d, C-5), 103.2 (d, C-1′), 79.0 (d, C-5′), 78.9 (d, C-3′), 75.3 (d, C-2′), 71.3 (d, C-4′), 62.4 (t, C-6′), 16.1 (t, C-8). ESI-MS *m/z* 357 $[M + Na]^+$. The above data were consistent with the literature [7].



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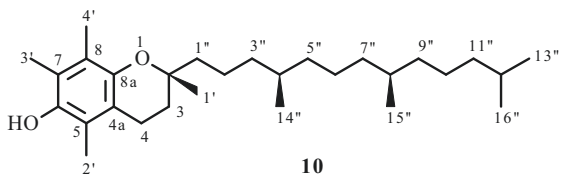

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5-(Methoxymethyl)-1*H*-pyrrole-2-carbaldehyde (4). Pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.47 (1H, s, CHO), 6.92 (1H, m, H-3), 6.22 (1H, m, H-4), 4.50 (2H, s, OCH_2), 3.39 (3H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, d, ppm): 178.9 (d, CHO), 137.6 (s, C-5), 132.7 (s, C-2), 121.5 (d, C-3), 109.8 (d, C-4), 67.0 (t, OCH_2), 58.4 (q, OCH_3).The above data were consistent with the literature [8].

4-Hydroxy-5-methylfuran-3-carboxylic Acid (5). Colorless needles. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm): 7.85 (1H, s, H-5), 2.30 (3H, s, 2-Me). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 170.2 (s, COOH), 151.8 (s, C-4), 145.8 (s, C-3), 142.9 (s, C-5), 140.4 (d, C-2), 14.5 (q, Me). ESI-MS *m/z:* 143 $[M + H]^+$, 165 $[M + Na]^+$. The above data were consistent with the literature [9].

Uracil (6). Light yellow solid, mp 335–337°C. ^{1}H NMR (400 MHz, C_5D_5N, δ, ppm, J/Hz): 13.10 (1H, s, NH), 12.45 (1H, s, NH), 7.51 (1H, d, J = 7.5, H-6), 5.80 (1H, d, J = 7.5, H-5). ^{13}C NMR (100 MHz, C_5D_5N, δ, ppm): 165.8 (s, C-4), 153.3 (s, C-2), 142.1 (d, C-5), 101.2 (d, C-6). The above data were consistent with the literature [10].

Benzoic Acid (7). White crystals, mp 122–123°C. The data were consistent with the literature [11].

Salicylic Acid (8). White crystals, mp 158–159°C. The data were consistent with the literature [12].

Thioacetic Anhydride (9). Colorless lamellar crystals (MeOH), mp 140–142°C. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm): 2.56 (6H, s, 2Me). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 176.3 (s, O–C=S), 29.8 (q, Me). The above data were consistent with the literature [13].

(2*R*,4a*R*,8a*R*)-3,4,4a,8a-Tetrahydro-4a-hydroxy-2,6,7,8a-tetramethyl-2-(4,8,12-trimethyltridecyl)-2*H*-chromene-5,8-dione (10). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) and ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) spectral data were consistent with the literature [14].

α-Tocopherol (11). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) and ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) spectral data were consistent with the literature [15].

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