

FLAVONOIDS IN *Sabina vulgaris* ANTOINE

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Seeds of *Sabina vulgaris* Antoine contain essential oil and has been studied for many years [1, 2]. However, the flavonoids of this plant have not been reported. We found this plant to be a rich source of flavonoids. Results are presented here.

The branches and leaves of this plant collected in the South mountains (Xinjiang region, PRC) in October 2001 were extracted with ethanol (5 times) at room temperature. The combined alcohol extracted was evaporated in vacuum. The condensed solution was diluted with water and successively treated with petroleum, ethyl acetate, and butanol. The solvents were removed to afford petroleum (53 g, chlorophyll), ethyl acetate 78 g, and butanol (124 g) fractions.

The ethyl acetate and butanol fractions were chromatographed over a silica-gel column separately with gradient elution by ethyl acetate – methanol (100:1-1:10). There were flavonoids in the ethyl acetate – methanol (2:1-1:3) fractions. All the fractions were combined to obtain 2.3 g flavonoids and the flavonoids were chromatographed over polyamide column with gradient elution by water- alcohol (10:1-1:9) to afford compounds 1–6. These compounds were identified using UV, mass, and PMR spectrum, chemical transformations, and comparison with authentic samples.

Hinokiflavone (1), C₃₀H₁₈O₁₀ (539, M⁺+1), mp 307–308°C, UV ($\lambda_{\max}$, nm): 268, 334 (MeOH), 270 (NaOMe), 390. IR (KBr, cm⁻¹): 3400, 1650, 1644 (Ar), 1604, 1580, 1500, 1380, 1360, 1170, 1040; 838. ¹H NMR (400 MHz, DMSO-d₆, δ , ppm, J/Hz): 8.01 (2H, d, J = 8.3, H-2', 6'), 7.96 (2H, d, J = 8.3, H-2'', 6''), 7.03 (2H, d, J = 8.3, H-3', 5'), 6.94 (2H, d, J = 8.3, H-3'', 5''), 6.85 (2H, s, H-3, 3''), 6.72 (1H, s, H-6), 6.49 (1H, s, H-8), 6.20 (1H, s, H-8'). ¹³C NMR (DMSO-d₆, 100 MHz, δ , ppm): 95.0 (C-8''), 95.4 (C-8), 99.2 (C-6), 102.9 (C-3''), 104.1 (C-3), 104.2 (C-10), 104.4 (C-10''), 115.7 (C-3', 5'), 116.3 (C-3'', 5''), 121.5 (C-1'''), 124.5 (C-1'), 124.9 (C-6''), 128.7 (C-2', 6'), 128.9 (C-2'', 6''), 153.1 (C-5'), 154.2 (C-9''), 157.4 (C-9), 157.7 (C-7''), 160.9 (C-5), 161.4 (C-4', 4''), 163.5 (C-7), 164.4 (C-2), 164.5 (C-2''), 182.1 (C-4), 182.4 (C-4'') [3, 4].

Amentoflavone (2), C₃₀H₁₈O₁₀ (539, M⁺+1), mp 246–249°C, UV ($\lambda_{\max}$, nm): 330, 319, 269, ¹H NMR (400 MHz, DMSO-d₆, δ , ppm, J/Hz): 5.98 (1H, d, J = 2.0, H-6), 6.19 (1H, s, H-6'), 6.25 (1H, d, J = 1.5, H-8), 6.58 (1H, s, H-3''), 6.62 (1H, d, H-3), 6.51 (2H, d, J = 9.0, H-3'', 5''), 6.94 (1H, d, J = 2.0, H-5'), 7.37 (2H, d, J = 9.0, H-2'', 6''), 7.81 (1H, d, J = 2.0, H-2'), 7.79 (1H, dd, J = 9.5, 2.0, H-6''); ¹³C NMR (100 MHz, CD₃OD, δ , ppm): 95.1 (C-8), 98.9 (C-6), 100.2 (C-6''), 103.4 (C-3''), 104.0 (C-3), 105.1 (C-8'), 105.3 (C-10''), 105.4 (C-10), 116.6 (C-3'', 5''), 117.3 (C-5'), 121.5 (C-1'''), 123.2 (C-1'), 123.3 (C-3'), 128.9 (C-2'), 129.3 (C-2'', 6''), 132.8 (C-6'), 156.3 (C-9''), 159.3 (C-9), 160.8 (C-4'), 162.5 (C-5, 5''), 163.1 (C-4''), 163.3 (C-7''), 165.9 (C-7), 166.0 (C-2''), 166.1 (C-2), 183.7 (C-4), 184.1 (C-4'') [5, 6].

Podocarpusflavone A (3), C₃₀H₁₈O₁₀ (552, M⁺), mp 234–236°C. UV ($\lambda_{\max}$, nm): 263, 330. ¹H NMR (400 MHz, DMSO-d₆, δ , ppm, J/Hz): 3.75 (3H, s, OCH₃), 6.21 (1H, d, J = 2.9, H-6), 6.35 (1H, s, H-6''), 6.44 (1H, d, J = 3.0, H-8), 6.80 (1H, s, H-3''), 6.76 (1H, s, H-3), 6.84 (2H, d, J = 9.0, H-3'', 5''), 7.10 (1H, d, J = 9.0, H-5'), 7.64 (2H, d, J = 9, H-2'', 6''), 7.96 (1H, d, J = 2.0, H-2'), 8.08 (1H, d, J = 2.9, H-6') [7, 8].

Apigenin (4), C₁₅H₁₀O₅ (271, M⁺+1), mp 347–348°C, UV spectrum ($\lambda_{\max}$, nm): 269, 300, 340; IR (KBr, cm⁻¹): 3330 (OH), 1650, 1610 (Ar), 1585, 1550, 1500, 1350, 1270, 1243, 1220; ¹H NMR (400 MHz, CDCl₃, δ , ppm, J/Hz): 6.19 (1H, d, H-3, J = 2.2, H-6), 6.47 (1H, d, J = 2.2, H-8), 6.77 (1H, s, H-3), 6.92 (2H, d, J = 8.8, H-3', 5'), 7.92 (2H, d, J = 8.8, H-2', 6'). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 95.1 (C-8), 99.8 (C-6), 103.5 (C-3), 104.6 (C-10), 116.9 (C-3', 5'), 122.3 (C-1'), 129.3 (C-2', 6'), 158.2 (C-9), 161.5 (C-4'), 164.6 (C-7), 165.0 (C-2), 182.7 (C-4) [9].

Luteolin 7-O- β -D-glucoside (5) C₂₁H₂₀O₁₁, mp 256–258°C, UV ($\lambda_{\max}$, nm): 255, 280, 348; IR (KBr, cm⁻¹): 3368, 1655 (C=O), 1592, 1526; ¹H NMR (400 MHz, DMSO-d₆, δ , ppm, J/Hz): 6.42 (1H, d, J = 2.1, H-6), 6.73 (1H, s, H-3), 6.77 (1H, d, J = 2.2, H-8), 6.88 (1H, d, J = 8.3, H-5'), 7.39 (1H, d, J = 2.1, H-2'), 7.42 (1H, dd, J = 8.4, 2.1, H-6'), 5.06 (1H, d, J = 7.2,

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H-1"). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 164.2 (C-2), 102.8 (C-3), 181.4 (C-4), 160.5 (C-5), 99.9 (C-6), 162.8 (C-7), 94.6 (C-8), 156.2 (C-9), 105.3 (C-10), 120.4 (C-1'), 113.7 (C-2'), 145.7 (C-3'), 150.3 (C-4'), 115.7 (C-5'), 119.3 (C-6'), 99.7 (Glu, C-1), 72.1 (Glu, C-2), 77.4 (Glu, C-3), 69.3 (Glu, C-4), 76.3 (Glu, C-5), 60.4 (Glu, C-6) [10].

Quercetin (6), $\text{C}_{15}\text{H}_{10}\text{O}_7$ (302, M^+), mp 252–253°C, UV spectrum (λ_{max} , nm): 257, 268, 370. IR (KBr, cm^{-1}): 3320 (OH), 1665 (C=O), 1618, 1575, 1520 (C=C), PMR spectrum (400 MHz, DMSO- d_6 , δ , ppm, J/Hz): 6.12 (1H, d, J=2.0, H-6), 6.35 (1H, d, J = 2.0, H-8), 6.85 (1H, d, J = 8.0, H-5'), 7.52 (1H, dd, J = 2.0, 8.0, H-6'), 7.67 (1H, d, J = 2.0, H-2') [11, 12].

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