

FLAVONOID COMPOUNDS FROM *Desmodium styracifolium* OF VIETNAMESE ORIGIN

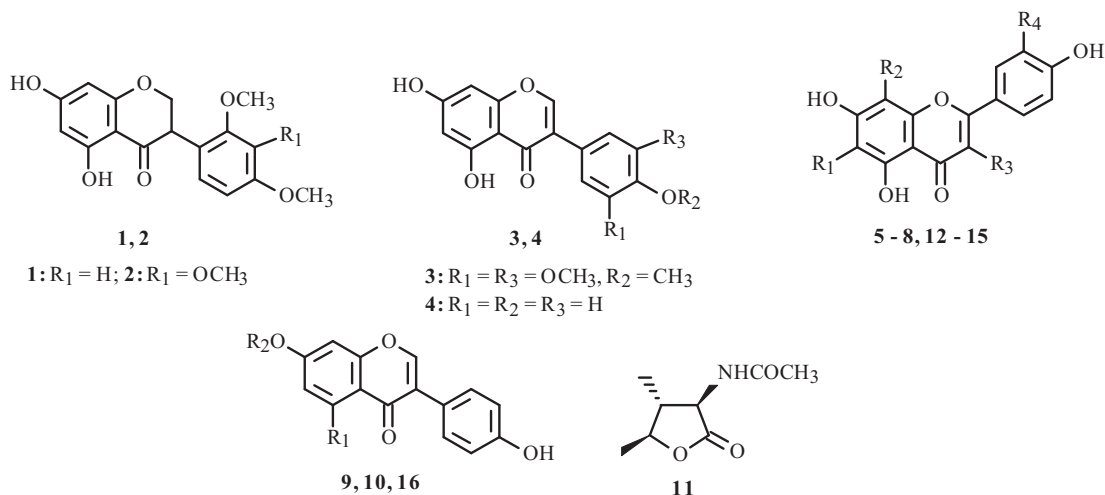
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Desmodium styracifolium (Osbeck) Merr. of the family Fabaceae is a small plant 40–80 cm in height and known in Vietnam by the name Kim tien thao. The whole plant is collected in Summer-Autumn and used as herbal medicines for urolithiasis, kidney problems, urethral infection, edematous nephritis, and hepatitis [1]. Previously isolated classes of compounds were volatile oil constituents, triterpenes, triterpenoid glycosides, flavonoids, flavonoid glycosides, and alkaloids [2–5]. The most systematic study [5] investigated the EtOH extract from the aerial parts of *D. styracifolium* from China, which found new isoflavanones, isoflavanone *O*-glycosides, and a coumaronochromone. The ethnomedicinal uses of the plant were supported by pharmacological studies on the prevention of kidney stones of polar constituents, flavonoid glycosides, triterpenoid glycosides, and polysaccharides, and the hypotensive action of an aqueous *D. styracifolium* extract [3, 4]. In the chemical study of the aerial parts of *D. styracifolium* originating in Vietnam, two isoflavanones, homoferreirin (**1**) and 5,7-dihydroxy-2',3',4'-trimethoxyisoflavanone (**2**), two isoflavones, panchovillin (**3**) and genistein (**4**), six flavonoid C-glucosides, isoorientin (**5**), isoschaftoside (**6**), schaftoside (**7**), isovitexin (**8**), isoorientin 3'-*O*-methyl ether (**12**), orientin (**13**), five flavonoid *O*-glucosides, genistin (**9**), ambonin (**10**), quercetin 3-*O*- β -D-glucopyranoside (**14**), astragalin (**15**), genistein 7-*O*- β -D-apiofuranosyl-(1 $\rightarrow$ 6)-*O*- β -D-glucopyranoside (**16**), and an amide, desmodilactone (**11**), were isolated. The structures of compounds **1–16** were determined by comparing their spectroscopic data (¹H and ¹³C NMR) with literature values [5–13]. To the best of our knowledge, compounds **3**, **6**, **9**, **10**, **12–16** were reported for the first time from *D. styracifolium*.

The air-dried aerial parts of *D. styracifolium* were purchased from Hanoi market of traditional medicines, Hanoi, Vietnam, in April 2005. A voucher specimen (No. HCTN 2005-4) is deposited in the Laboratory of Chemistry of Natural Products, Faculty of Chemistry, College of Natural Science, Vietnam National University, Hanoi, Vietnam. The plant material (3.0 kg) was extracted with MeOH by percolation at room temperature (3 times, for 3 days each) and sequentially fractionated using solvents of increasing polarity to give *n*-hexane (62.3 g), CH₂Cl₂ (6.4 g), EtOAc (6.9 g), and 1-BuOH-soluble (83.4 g) fractions. The CH₂Cl₂-soluble fraction (6.4 g) was submitted to sequential chromatography on a gradient silica gel column (*n*-hexane–EtOAc, 4:1, 2:1, and 1:1) and an octadecyl silica (ODS) gel column (MeOH–H₂O, 7:3), followed by purification on ODS gel preparative high-performance liquid chromatography (HPLC) (MeOH–H₂O, 7:3) to afford a mixture of **1** and **2** (16.0 mg), **3** (9.0 mg), and **4** (5.1 mg). The 1-BuOH fraction (83.4 g) was fractionated by column chromatography on Diaion HP-20, eluting with H₂O, MeOH–H₂O, 2:3 and 3:2, and MeOH, into four corresponding pooled fractions, H₂O fraction, 40% MeOH–H₂O fraction, 60% MeOH–H₂O fraction, and MeOH fraction. The 40% (20.9 g) and 60% MeOH–H₂O (6.5 g) fractions were sequentially fractionated by the same procedure: 1) chromatography on a silica gel column eluting with stepwise gradients CHCl₃–MeOH, 9:1, 4:1, and 7:3 and CHCl₃–MeOH–H₂O 15:6:1; 2) chromatography on an ODS gel column eluting with MeOH–H₂O, 2:3; 3) droplet countercurrent chromatography (DCCC); the lower and upper phases of a solvent mixture of CHCl₃–MeOH–H₂O–1-PrOH, 9:12:8:2 were used for the stationary and mobile phases, respectively; and finally 4) purification on ODS gel preparative HPLC eluting with MeOH–H₂O, 3:7 or 2:3. Compounds **5** (5.0 mg), **6** (52.4 mg), **7** (27.2 mg), **8** (102 mg), **9** (125 mg), **10** (5.0 mg), and **11** (310 mg) were isolated from the 40% MeOH–H₂O fraction. Compounds **6** (6.0 mg), **7** (39.9 mg), **12** (14.6 mg), **13** (13.7 mg), **14** (3.8 mg), **15** (86.5 mg), and **16** (140 mg) were isolated from the 60% MeOH–H₂O fraction.

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5: R₁ = β -Glc, R₂ = R₃ = H, R₄ = OH; 6: R₁ = α -Ara, R₂ = β -Glc, R₃ = R₄ = H; 7: R₁ = β -Glc, R₂ = α -Ara, R₃ = R₄ = H
 8: R₁ = β -Glc, R₂ = R₃ = R₄ = H; 9: R₁ = OH, R₂ = β -Glc; 10: R₁ = H, R₂ = β -Api-(1 $\rightarrow$ 6)- β -Glc
 12: R₁ = β -Glc, R₂ = R₃ = H, R₄ = OCH₃; 13: R₁ = R₃ = H, R₂ = β -Glc, R₄ = OH
 14: R₁ = R₂ = H, R₃ = *O*- β -Glc, R₄ = OH; 15: R₁ = R₂ = R₄ = H, R₃ = *O*- β -Glc
 16: R₁ = OH, R₂ = β -Api-(1 $\rightarrow$ 6)- β -Glc

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