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# Studies on the Constituents of *Sophora flavescens* AITON. II[1)]

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Two flavanones, kushenol A (**1**) and kushenol B (**2**), one flavonol, kushenol C (**3**), one chalcone, kushenol D (**4**), and one pterocarpan, kushenin (**5**), were isolated from the dry roots of *Sophora flavescens* AITON (Leguminosae). Their structures were elucidated on the basis of elemental analyses and spectral data.

**Keywords**——*Sophora flavescens*; flavanone; flavonol; chalcone; pterocarpan; kushenol A; kushenol B; kushenol C; kushenol D; kushenin

The oriental crude drug "Kushen (苦参)," dry roots of *Sophora flavescens* AITON (Leguminosae), has been used as a stomachic, an antifebrile, an anodyne and an anthelmintic. As constituents of Kushen, alkaloids,[2,3)] pterocarpans[4)] and flavonoids[5–7)] have so far been isolated. We previously reported the structures[1,8)] and biological activities[9)] of the constituents of *Sophora flavescens*. In the present paper we describe the isolation from Kushen and the structural elucidation of five new minor constituents, named kushenol A (**1**), kushenol B (**2**), kushenol C (**3**), kushenol D (**4**) and kushenin (**5**) (Chart 1). These five new constituents were isolated from the ethyl acetate layer of the methanol extract as shown in Chart 2.

Kushenol A (**1**) was obtained as pale yellow needles from benzene, mp 172—174 °C. $[\alpha]_D^{21}$ −115.6°. $M^+$ 408, $C_{25}H_{28}O_5$. The Gibbs reaction and Mg–HCl reaction of **1** were positive. The infrared (IR) spectrum of **1** showed the presence of hydroxyl groups (3600 and 3200 $cm^{-1}$) and a conjugated carbonyl group (1640 $cm^{-1}$). The ultraviolet (UV) spectra of **1** in methanol (242, 295 and 340 nm) and in the presence of shift reagents suggested the presence of a 5,7-dihydroxyflavanone moiety.[10)] The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **1** showed signals due to a hydrogen-bonded hydroxyl proton ($\delta$: 12.56), H-2 [$\delta$: 5.74 (1H, dd, $J$=12.0, 4.5 Hz)] and H-3 [$\delta$: 2.88—3.20 (2H, m)] of the flavanone, a lavandulyl(5-methyl-2-isopropenyl-hex-4-enyl) group[6,7)] [$\delta$: 1.48 (3H, s, $CH_3$), 1.56 (3H, s, $CH_3$), 1.66 (3H, s, $CH_3$), 1.96—2.17 (3H, m), 2.64 (2H, m, H-1′), 4.60 (2H, br s, H-9′′) and 5.00 (1H, br t, $J$=7.0 Hz, H-4′′)] and five aromatic protons [$\delta$: 6.01 (1H, s), 6.92—7.61 (4H, m)]. In the mass spectrum (MS) of **1**, a fragment, $m/z$ 285 [$M^+ - 123$ ($C_9H_{15}$)], suggested the presence of a lavandulyl group, and a fragment, $m/z$ 120 ($C_8H_8O$), due to the retro Diels–Alder cleavage of the flavanone, indicated that the B ring of **1** has one hydroxyl group and no lavandulyl group. The carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum of **1** showed the presence of four oxygenated aromatic carbons ($\delta$: 154.7, 161.8, 163.1, 165.3) and one carbonyl carbon ($\delta$: 197.7), so this flavanone has three hydroxyl groups at C-5, C-7 and in the B ring. Chemical shifts and splitting patterns of the B ring signals in the $^1$H-NMR and $^{13}$C-NMR[11)] spectra indicated that the hydroxyl group is located at C-2′. In the non-decoupled $^{13}$C-NMR spectrum with nuclear Overhauser effect (NOE), a signal at $\delta$: 96.6 was observed as a double doublet ($J$=161.1, 7.3 Hz), but was changed to a doublet ($J$=161.1 Hz) by the addition of deuterium oxide. This experiment indicated that the C-6 carbon has a $^{13}$C-$^1$H long-range coupling with the C-5 hydroxy proton[12)] and carried one proton. Thus, the

lavandulyl group must be located at C-8. In the circular dichroism (CD) spectrum, **1** showed a positive maximum at 311 nm ([$\theta$] +1665) and a negative maximum at 290 ([$\theta$] −5921), so the absolute configuration at C-2 was confirmed as *S*.[13,14] Thus, the structure of **1** was concluded to be (−)-(2*S*)-8-lavandulyl-5,7,2′-trihydroxyflavanone.

Kushenol B (**2**) was obtained as pale yellow needles from benzene–acetone, mp 147—150 °C. $[\alpha]_D^{21}$ −40.2°. $M^+$ 492, $C_{30}H_{36}O_6$. The Mg–HCl reaction was positive. The IR spectrum of **2** showed the presence of hydroxyl groups (3500 and 3200 $cm^{-1}$) and a conjugated carbonyl group (1645 $cm^{-1}$). The UV spectra of **2** in methanol (295 and 333 nm) and in the presence of shift reagents suggested the presence of a 5,7-dihydroxyflavanone moiety.[10] The $^1$H-NMR spectrum of **2** showed signals due to a hydrogen-bonded hydroxyl proton ($\delta$: 12.47), a lavandulyl group, a 3-methyl-2-butenyl group [$\delta$: 1.64 (3H, s), 1.76 (3H, s), 3.38 (2H, br d, $J$=7.0 Hz) and 5.15 (1H, br t, $J$=7.0 Hz)], three aromatic protons [$\delta$: 6.48 (1H, dd, $J$=9.0, 2.5 Hz), 6.52 (1H, d, $J$=2.5 Hz) and 7.42 (1H, d, $J$=9.0 Hz)], a H-2 [$\delta$: 5.68 (1H, dd, $J$=12.0, 4.5 Hz)] and H-3 [$\delta$: 2.52—3.10 (2H, m)] of the flavanone. These chemical shifts and the splitting patterns of the three aromatic protons indicated the presence of a 2,4-dihydroxyphenyl moiety as the B ring of **2**, as in norkurarinone.[6] The $^{13}$C-NMR spectrum showed five oxygenated aromatic carbons ($\delta$: 156.1, 159.4, 160.0, 160.2, 162.6) and one carbonyl carbon ($\delta$: 198.4), so this flavanone has four hydroxyl groups. In the MS of **2**, a fragment, *m/z* 136 ($C_8H_8O_2$), due to the retro Diels–Alder cleavage of the flavanone, suggested that the B ring of **2** has two hydroxyl groups, in accordance with the $^1$H-NMR spectrum. Thus, the A ring of **2** has one lavandulyl, one 3-methyl-2-butenyl and two hydroxyl groups. From the above data, **2** was considered to be a 5,7,2′,4′-tetrahydroxyflavanone derivative. Many flavanones of Kushen have a lavandulyl group at C-8,[6,7] so the positions of the lavandulyl and 3-methyl-2-butenyl group of **2** are presumed to be at C-8 and C-6, respectively, through there is no direct evidence. In the CD spectrum, **2** showed a positive maximum at 340 nm ([$\theta$] +623) and a negative maximum at 293 nm ([$\theta$] −5031), so the absolute configuration at C-2 was confirmed as *S*.[13,14] Thus, the structure of **2** was presumed to be (−)-(2*S*)-8(or 6)-lavandulyl-6(or 8)-(3-methyl-2-butenyl)-5,7,2′,4′-tetrahydroxyflavanone.

Kushenol C (**3**) was obtained as a yellow amorphous powder. $[\alpha]_D^{21}$ −8.8°. $M^+$ 438, $C_{25}H_{26}O_7$. The Mg–HCl reaction was positive. The IR spectrum of **3** showed the presence of hydroxyl groups (3300 $cm^{-1}$) and a conjugated carbonyl group (1630 $cm^{-1}$). The UV spectra of **3** in methanol (269, 308 and 363 nm) and in the presence of shift reagents suggested the presence of a 5,7-dihydroxyflavonol moiety.[10] The $^1$H-NMR spectrum showed signals due to a hydrogen-bonded hydroxyl proton ($\delta$: 12.57) and a lavandulyl group, as in the case of **1** and **2**. In the $^{13}$C-NMR spectrum, the signals ($\delta$: 142.2, 149.3 and 179.6) were assigned to C-2, C-3 and C-4 of the flavonol, respectively.[14] In the non-decoupled $^{13}$C-NMR spectrum with NOE, a $^{13}$C–$^1$H long-range coupling between the C-6 carbon and C-5 hydroxyl proton was observed,[12] and C-6 carried one proton, as in **1**. By comparison of the chemical shifts and the splitting patterns of the $^1$H- and $^{13}$C-NMR spectra with those of **1** and **2**, it was confirmed that **3** had the same A ring moiety as **1**, and the same B ring moiety as **2**. Thus, the structure of **3** was concluded to be (−)-8-lavandulyl-5,7,2′,4′-tetrahydroxyflavonol.

Kushenol D (**4**) was obtained as a yellow amorphous powder. $M^+$ 452, $C_{27}H_{32}O_6$. The Mg–HCl reaction was negative. The IR spectrum of **4** showed the presence of hydroxyl groups (3400 $cm^{-1}$) and a conjugated carbonyl group (1620 $cm^{-1}$). The UV spectra of **4** in methanol (255 and 383 nm) and in the presence of shift reagents suggested the presence of a 4,2′-dihydroxychalcone moiety.[10] The $^1$H-NMR spectrum of **4** showed signals due to a hydrogen-bonded hydroxyl proton ($\delta$: 14.38), a lavandulyl group, two methoxyl groups ($\delta$: 3.69 and 3.71), two olefinic protons [$\delta$: 8.30 (1H, d, $J$=15.0 Hz) and 8.70 (1H, d, $J$=15.0 Hz)] and four aromatic protons [$\delta$: 6.28 (1H, s), 6.73 (1H, d, $J$=2.5 Hz), 6.80 (1H, dd, $J$=9.0,

2.5 Hz) and 7.75 (1H, d, $J=9.0$ Hz)]. This spectrum was very similar to that of kuraridin.[6] A comparison with the $^{13}$C-NMR spectrum of 2,6,2′,4′-tetrahydroxy-6′-methoxychalcone[14] indicated that **4** is a 2,4,2′,4′-tetrahydroxy-6′-methoxychalcone derivative. In the MS of **4**, the fragments, $m/z$ 383 [$M^+ - 69$ ($C_5H_9$)], 329 [$M^+ - 123$ ($C_9H_{15}$)], 233 [383 − 150 ($C_9H_{10}O_2$)] and 179 [329 − 150 ($C_9H_{10}O_2$)], suggested that the A ring has a lavandulyl, a methoxyl and two hydroxyl groups, and the B ring has a hydroxyl group. In NOE experiments, irradiation at two methoxyl signals ($\delta$: 3.69 and 3.71) increased the intensity of the H-5′ ($\delta$: 6.28), H-3 ($\delta$: 6.73) and H-α ($\delta$: 8.30) signals, so methoxyl group must be located at C-2 and C-6′ of the chalcone. Thus, the structure of **4** was concluded to be 2,6′-dimethoxy-3′-lavandulyl-4.2′,4′-trihydroxychalcone.

Kushenin (**5**) was obtained as colorless needles from chloroform, mp 230—232 °C. $M^+$ 286, $C_{16}H_{14}O_5$. The Mg–HCl reaction was negative. The IR spectrum of **5** showed the presence of hydroxyl groups (3400 cm$^{-1}$). The UV spectrum of **5** in methanol (233, 286 and

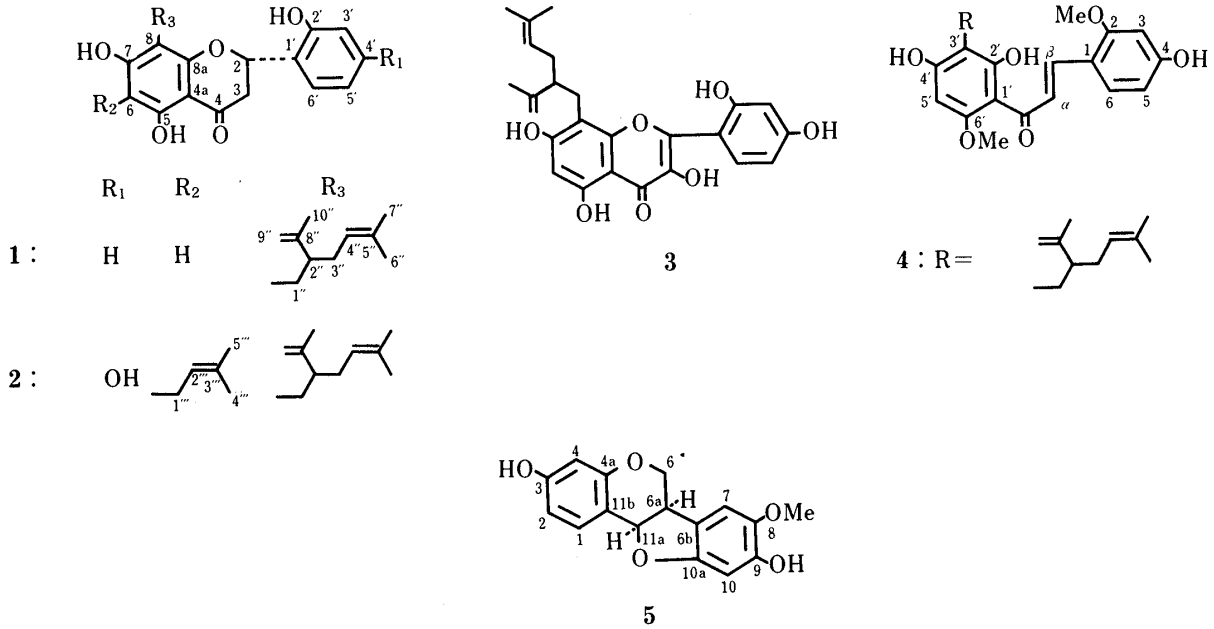


Chart 1

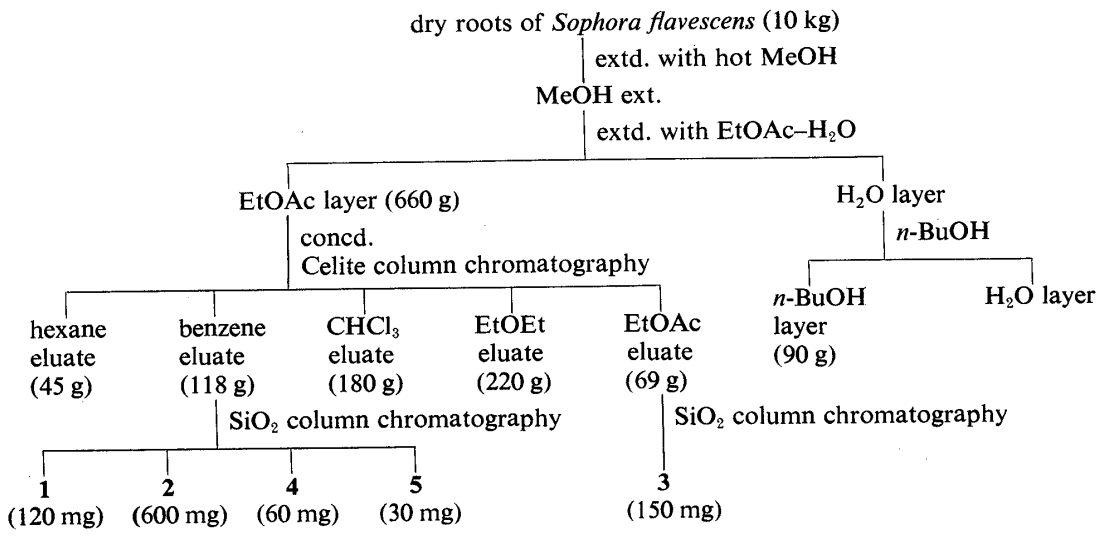


Chart 2

TABLE I. $^{13}$C-NMR Data for **1**, **2**, **3**, **4** and **5** (22.5 MHz)

| Carbon | **1**[a] | **2**[a] | **3**[a] | **4**[b] | **5**[a] |
|---|---|---|---|---|---|
| 1 | | | | 108.8 (s) | 133.0 (d) |
| 2 | 75.5 (d) | 75.5 (d) | 149.3 (s) | 161.7 (s) | 110.6 (d) |
| 3 | 42.7 (t) | 43.1 (t) | 142.2 (s) | 99.9 (d) | 159.7 (s) |
| 4 | 197.7 (s) | 198.4 (s) | 179.6 (s) | 161.1 (s) | 104.0 (d) |
| 4a | 103.3 (s) | 103.6 (s) | 106.3 (s) | | 157.8 (s) |
| 5 | 163.1 (s) | 160.0 (s) | 156.0 (s) | 108.8 (d) | |
| 6 | 96.6 (d) | 108.5 (s) | 98.5 (d) | 125.5 (d) | 67.2 (t) |
| 6a | | | | | 41.3 (d) |
| 6b | | | | | 118.0 (s) |
| 7 | 165.3 (s) | 162.6 (s) | 162.3 (s) | | 110.5 (d) |
| 8 | 108.0 (s) | 107.6 (s) | 103.9 (s) | | 142.8 (s) |
| 8a | 161.8 (s) | 160.2 (s) | 161.7 (s) | | |
| 9 | | | | | 148.8 (s) |
| 10 | | | | | 98.8 (d) |
| 10a | | | | | 155.2 (s) |
| 11a | | | | | 79.0 (s) |
| 11b | | | | | 113.2 (s) |
| 1′ | 126.8 (s) | 118.1 (s) | 114.2 (s) | 108.2 (s) | |
| 2′ | 154.7 (s) | 156.1 (s) | 159.0 (s) | 162.7 (s) | |
| 3′ | 116.3 (d) | 103.6 (d) | 106.3 (d) | 117.0 (s) | |
| 4′ | 130.0 (d) | 159.4 (s) | 161.2 (s) | 164.0 (s) | |
| 5′ | 120.7 (d) | 107.9 (d) | 108.3 (d) | 91.6 (d) | |
| 6′ | 127.4 (d) | 128.6 (d) | 129.4 (d) | 166.7 (s) | |
| 1″ | 27.8 (t) | 28.3 (t) | 28.1 (t) | 27.8 (t) | |
| 2″ | 47.8 (d) | 47.8 (d) | 47.9 (d) | 47.2 (d) | |
| 3″ | 32.0 (t) | 31.8 (t) | 32.1 (t) | 31.9 (t) | |
| 4″ | 124.5 (d) | 124.4 (d) | 124.1 (d) | 124.6 (d) | |
| 5″ | 131.6 (s) | 131.7 (s) | 131.6 (s) | 130.8 (s) | |
| 6″ | 17.8 (q) | 17.8 (q) | 17.8 (q) | 17.8 (q, | |
| 7″ | 25.7 (q) | 25.8 (q) | 25.8 (q) | 25.6 (q) | |
| 8″ | 149.2 (s) | 149.3 (s) | 148.9 (s) | 149.2 (s) | |
| 9″ | 111.1 (t) | 111.1 (t) | 111.5 (t) | 110.7 (t) | |
| 10″ | 19.3 (q) | 19.6 (q) | 19.2 (q) | 19.1 (q) | |
| 1‴ | | 21.8 (t) | | | |
| 2‴ | | 123.4 (d) | | | |
| 3‴ | | 130.0 (s) | | | |
| 4‴ | | 17.8 (q) | | | |
| 5‴ | | 25.8 (q) | | | |
| OMe | | | | 55.7 (q×2) | 57.7 (q) |
| C=O | | | | 193.5 (s) | |
| α | | | | 130.3 (d) | |
| β | | | | 138.3 (d) | |

a) In acetone-$d_6$. b) In pyridine-$d_5$.

298 nm) was similar to those of pterocarpans.[4] The $^1$H- and $^{13}$C-NMR spectra of **5** showed signals due to a methoxy group [$\delta$: 3.76 (3H, s) and 57.7 (q)], and were also very similar to those of pterocarpin.[11,15] In the NOE experiments, irradiation at the methoxyl signal ($\delta$: 3.76) increased the intensity (18%) of the H-7 ($\delta$: 6.96, s) signal, so the methoxyl group must be at C-8. The optical rotatory dispersion (ORD) curve of **5** was similar to those of (−)-pterocarpin[16] and melilotocarpans.[17] Therefore, the absolute configuration of **5** was confirmed as 6a*R* and 11a*R*. Thus, the structure of **5** was concluded to be (6a*R*, 11a*R*)-3,9-dihydroxy-8-methoxypterocarpan.

## Experimental

All melting points were determined on a Yanaco MP-500 micro melting point apparatus and are uncorrected. The IR spectra were recorded on a JASCO A-202 grating infrared spectrophotometer, and the UV spectra were recorded on a Shimadzu UV-360 recording spectrophotometer. The NMR spectra ($^1$H-NMR 89.55 and 399.65 MHz; $^{13}$C-NMR 22.5 MHz) were recorded on a JEOL FX-90Q and JEOL GX-400 NMR spectrometer with tetramethylsilane as an internal standard ($\delta$ value; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad). The MS were recorded on a JEOL JMS-D 100 mass spectrometer. The optical rotations were determined on a JASCO DIP-140 digital polarimeter. The CD and ORD spectra were recorded on a JASCO J-20A spectropolarimeter. Silica gel $60F_{254}$ (Merck) was used for thin layer chromatography (TLC) and detection was achieved by illumination with an ultraviolet lamp, by spraying 3% $FeCl_3$ ethanol solution or by spraying 50% $H_2SO_4$ aq. followed by heating. For column chromatography, Silica gel 60 (Merck) was used.

**Extraction and Separation**——The dry cut roots (10 kg) of *Sophora flavescens* AITON (commercial product from He-bei-sheng, 河北省, China) were extracted three times with MeOH under reflux. The MeOH extract was concentrated under reduced pressure, and the concentrate was suspended in water. The suspension was extracted with ethyl acetate and *n*-butanol, successively. The ethyl acetate-soluble fraction was concentrated *in vacuo* to afford a residue (660 g), which was fractionated by Celite column chromatography with hexane, benzene, chloroform, diethyl ether and ethyl acetate successively; the yields were 45 g, 118 g, 180 g, 220 g and 69 g, respectively. The benzene eluate was chromatographed repeatedly on a silica gel column to give **1** (120 mg), **2** (600 mg), **4** (60 mg) and **5** (30 mg). The ethyl acetate eluate was also chromatographed repeatedly on a silica gel column to give **3** (150 mg).

**Kushenol A (1)**——Pale yellow needles from benzene, mp 172—174 °C, $[\alpha]_D^{21}$ −115.6° ($c$=0.40, MeOH). The Gibbs reaction and Mg–HCl reaction were positive. MS $m/z$ (rel. int., %): 408 ($M^+$, 12), 286 (22), 285 (100), 267 (56), 165 (84), 120 (30). IR (KBr) cm$^{-1}$: 3600, 3200, 1640, 1605, 880, 745. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 242 (3.93), 295 (4.25), 340 (3.55); $\lambda_{max}^{MeOH-AlCl_3}$ nm: 315, 390; $\lambda_{max}^{MeOH-AlCl_3/HCl}$ nm: 313, 389; $\lambda_{max}^{MeOH-AcONa}$ nm: 295, 334; $\lambda_{max}^{MeOH-AcONa/H_3BO_3}$ nm: 294, 334. $^1$H-NMR (acetone-$d_6$) $\delta$: 1.48 (3H, s, $CH_3$), 1.56 (3H, s, $CH_3$), 1.66 (3H, s, $CH_3$), 1.96—2.17 (3H, m), 2.64 (2H, m, H-1″), 2.88—3.20 (2H, m, H-3), 4.60 (2H, br s, H-9″), 5.00 (1H, br t, $J$=7.0 Hz, H-4″), 5.74 (1H, dd, $J$=12.0, 4.5 Hz, H-2), 6.01 (1H, s, H-6), 6.92—7.61 (4H, m), 12.56 (1H, br s, $C_5$-OH). CD ($c=2.2\times10^{-4}$, MeOH) $[\theta]^{20}$ (nm): +1665 (311) (positive maximum); −5921 (290) (negative maximum). *Anal.* Calcd for $C_{25}H_{28}O_5$: C, 73.51; H, 6.91. Found: C, 73.58; H, 6.93.

**Kushenol B (2)**——Pale yellow needles from benzene–acetone, mp 147—150 °C. $[\alpha]_D^{21}$ −40.2° ($c$=0.39, MeOH). The Mg–HCl reaction was positive. MS $m/z$ (rel. int., %): 492 ($M^+$, 15), 369 (100), 351 (40), 313 (21), 295 (64), 233 (60), 177 (85), 136 (15), 123 (15). IR (KBr) cm$^{-1}$: 3500, 3200, 1645, 1600, 1520, 980, 840. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 295 (3.66), 333 (3.09); $\lambda_{max}^{MeOH-AlCl_3}$ nm: 315, 389; $\lambda_{max}^{MeOH-AlCl_3/HCl}$ nm: 310, 385; $\lambda_{max}^{MeOH-AcONa}$ nm: 296, 340; $\lambda_{max}^{MeOH-AcONa/H_3BO_3}$ nm: 295, 337. $^1$H-NMR (acetone-$d_6$) $\delta$: 1.48 (3H, s, $CH_3$), 1.54 (3H, s, $CH_3$), 1.64 (6H, s, $CH_3\times2$), 1.76 (3H, s, $CH_3$), 2.52—3.10 (2H, m, H-3), 2.92 (2H, m, H-1″), 3.38 (2H, br d, $J$=7.0 Hz, H-1‴), 4.62 (2H, br s, H-9″), 4.96 (1H, br t, $J$=7.0 Hz, H-4″), 5.15 (1H, br t, $J$=7.0 Hz, H-2‴), 5.68 (1H, dd, $J$=12.0, 4.5 Hz, H-2), 6.48 (1H, dd, $J$=9.0, 2.5 Hz, H-5′), 6.52 (1H, d, $J$=2.5 Hz, H-3′), 7.42 (1H, d, $J$=9.0 Hz, H-6′), 8.98 (1H, br s, OH), 9.34 (1H, br s, OH), 9.62 (1H, br s, OH), 12.47 (1H, br s, $C_5$-OH). CD ($c=2.2\times10^{-4}$, MeOH) $[\theta]^{20}$ (nm): +623 (340) (positive maximum); −5031 (293) (negative maximum). *Anal.* Calcd for $C_{30}H_{36}O_6\cdot1/2H_2O$: C, 72.50; H, 7.35. Found: C, 72.74; H, 7.16.

**Kushenol C (3)**——Yellow amorphous powder. $[\alpha]_D^{21}$ −8.8° ($c$=0.28, MeOH). The Mg–HCl reaction was positive. MS $m/z$ (rel. int., %): 438 ($M^+$, 14), 423 (7), 315 (43), 165 (14), 149 (22), 124 (85). IR (KBr) cm$^{-1}$: 3300, 1630, 1600, 1560. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 269 (4.35), 308 (sh), 363 (4.11); $\lambda_{max}^{MeOH-MeONa}$ nm: 282, 323, 421; $\lambda_{max}^{MeOH-AlCl_3}$ nm: 271, 308 (sh), 355 (sh), 426; $\lambda_{max}^{MeOH-AlCl_3/HCl}$ nm: 270, 308 (sh), 355 (sh), 426; $\lambda_{max}^{MeOH-AcONa}$ nm: 273, 396. $^1$H-NMR (acetone-$d_6$) $\delta$: 1.50 (3H, s, $CH_3$), 1.59 (3H, s, $CH_3$), 1.72 (3H, s, $CH_3$), 4.58 (2H, br s, H-9″), 5.00 (1H, br t, $J$=7.0 Hz, H-4″), 6.26 (1H, s, H-6), 6.30 (1H, d, $J$=2.5 Hz, H-3′), 6.42 (1H, dd, $J$=9.0, 2.5 Hz, H-5′), 7.70 (1H, d, $J$=9.0 Hz, H-6′), 12.57 (1H, br s, $C_5$-OH). *Anal.* Calcd for $C_{25}H_{26}O_7$: C, 68.48; H, 5.98. Found: C, 68.40; H, 6.02.

**Kushenol D (4)**——Yellow amorphous powder. The Mg–HCl reaction was negative. MS $m/z$ (rel. int., %): 452 ($M^+$, 10), 383 (6), 329 (25), 233 (6), 179 (100). IR (KBr) cm$^{-1}$: 3400, 1620, 1580. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 255 (3.30). 383 (3.90): $\lambda_{max}^{MeOH-AlCl_3}$ nm: 386, 410; $\lambda_{max}^{MeOH-AlCl_3/HCl}$ nm: 385, 410: $\lambda_{max}^{MeOH-AcONa}$ nm: 388; $\lambda_{max}^{MeOH-AcONa/H_3BO_3}$ nm: 386. $^1$H-NMR (pyridine-$d_5$) $\delta$: 1.61 (3H, s, $CH_3$), 1.64 (3H, s, $CH_3$), 1.98 (3H, s, $CH_3$), 3.69 (3H, s, $OCH_3$), 3.71 (3H, s, $OCH_3$), 4.92 (2H, br s, H-9″), 5.35 (1H, br t, $J$=7.0 Hz, H-4″), 6.28 (1H, s, H-5′), 6.73 (1H, d, $J$=2.5 Hz, H-3), 6.80 (1H, dd, $J$=9.0, 2.5 Hz, H-5), 7.75 (1H, d, $J$=9.0 Hz, H-6), 8.30 (1H, d, $J$=15.0 Hz, H-$\alpha$), 8.70 (1H, d, $J$=15.0 Hz, H-$\beta$), 14.38 (1H, br s, $C_2$-OH). *Anal.* Calcd for $C_{27}H_{32}O_6\cdot1/2H_2O$: C, 70.28; H, 7.16. Found: C, 70.25; H, 7.15.

**Kushenin (5)**——Colorless needles from $CHCl_3$, mp 230—232 °C. The Mg–HCl reaction was negative. MS $m/z$ (rel. int., %): 286 ($M^+$, 100), 285 (30), 271 (35), 177 (14), 164 (24), 147 (26), 134 (30). IR (KBr) cm$^{-1}$: 3400, 1630, 1600, 1510, 1500, 850. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 233 (3.38), 286 (3.26), 298 (3.30). $^1$H-NMR (acetone-$d_6$) $\delta$: 3.50—3.70 (2H, m, H-$6_{ax}$, H-6a), 3.76 (3H, s, $OCH_3$), 4.24 (1H, m, H-$6_{eq.}$), 5.38 (1H, d, $J$=6.0 Hz, H-11a), 6.30 (1H, s, H-10), 6.32 (1H, d, $J$=2.5 Hz, H-4), 6.50 (1H, dd, $J$=9.0, 2.5 Hz, H-2), 6.96 (1H, s, H-7), 7.28 (1H, d, $J$=9.0 Hz, H-1), 7.52 (1H, br s, OH), 8.60 (1H, br s, OH). ORD ($c=1.085\times10^{-3}$, MeOH) $[M]^{20}$ (nm): −105 (312) (peak), −2741 (285) (trough),

−2161 (272) (peak), −5588 (241) (trough). *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.09; H, 4.82.

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