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Chemical and Chemotaxonomical Studies on Filices. LI.[1] Chemical Studies on the Constituents of Costa Rican Ferns. (3)[2]

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The constituents of three Costa Rican ferns of Pteridaceae were investigated. From *Jamesonia scammanae* A. TRYON, a new pterosin-type compound (I), named jamesonin, along with two pterosin derivatives and six *ent*-kaurane-type diterpene derivatives were isolated, and I was established as (2*R*,3*R*)-3-hydroxy-6-(2-hydroxyethyl)-2,7-bishydroxymethyl-2,5-dimethylindan-1-one by spectroscopic methods. From *Dicksonia gigantea* KARST., two known pterosin derivatives were isolated, and from *Paesia anfractuosa* C. CHR., two flavonol glycosides.

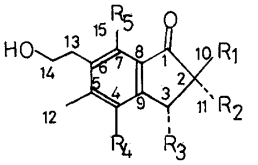
Keywords——*Jamesonia scammanae*; *Dicksonia gigantea*; *Paesia anfractuosa*; Pteridaceae; pterosin-type sesquiterpene; *ent*-kaurane-type diterpene; flavonol glycoside; ^{13}C-NMR

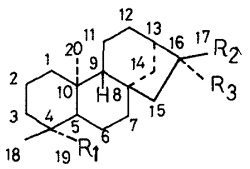
As a continuation of our chemical and chemotaxonomical studies of filices, the constituents of three Costa Rican ferns of Pteridaceae were investigated. This paper deals with the results of the investigation including the structural elucidation of a new compound.

(1) *Jamesonia scammanae* A. TRYON

From this fern, a new pterosin-type sesquiterpene (I), named jamesonin, was isolated along with pterosin S (II),[3] pterosin B (III)[4] and six known *ent*-kaurane type diterpenes: 16α-hydroxy-*ent*-kaurane (IV),[5] *ent*-kaur-16-en-19-oic acid (V),[6] *ent*-kaur-15-en-19-oic acid (VI),[6b,7] 16α-hydroxy-*ent*-kauran-19-oic acid (VII),[8] 16α,17-dihydroxy-*ent*-kaurane (VIII)[9] and 16β,17-dihydroxy-*ent*-kaurane (IX).[9]

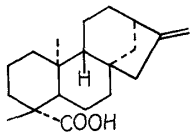
Jamesonin (I), $C_{15}H_{20}O_5$, colorless amorphous powder, $[\alpha]_D^{24}$ +9.6°, showed ultraviolet (UV) [λ_{max}^{MeOH} nm (log ε): 218 (4.31), 261.5 (3.91), 304 (3.23)] absorptions characteristic of a pterosin-type compound. In the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum, signals due to one methyl group at C-2 at $\delta_{Pyr.-d_5}$ 1.33 (3H, s), one aromatic methyl group at C-5 at δ 2.38 (3H, s),[3] one hydroxyethyl group at C-6 at δ 3.32 (2H, t, J=7 Hz) and 4.05 (2H, t, J=7 Hz), one hydroxymethyl group at δ 4.18 (2H, AB q, J=10 Hz), one carbinyl proton at C-3 at δ 5.13 (1H, s), one aromatic hydroxymethyl group at C-7 at δ 5.46 (2H, AB q, J=12 Hz)[3] and one aromatic proton at C-4 at δ 7.59 (1H, s) were observed. The spectrum differs from that of pterosin S (II) in the following respects, that is, the signal due to a methyl group at C-2 is found as a singlet and the signal due to an additional hydroxymethyl group is observed at δ 4.18, suggesting that I is a derivative of pterosin S bearing a hydroxymethyl group at C-2. This conclusion is supported by comparing the ^{13}C-NMR spectrum of I with that of pterosin S (II). The ^{13}C-NMR signals assigned to a hydroxymethyl group and a methyl group at C-2 in



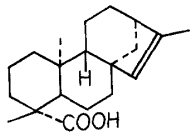


	R_1	R_2	R_3	R_4	R_5
jamesonin (I):	CH_3	CH_2OH	OH	H	CH_2OH
pterosin S (II):	CH_3	H	OH	H	CH_2OH
pterosin B (III):	CH_3	H	OH	H	CH_3
onitin (XO):	CH_3	CH_3	H	OH	CH_3
pterosin D (XII):	CH_3	CH_3	OH	H	CH_3
pterosin L:	CH_3	CH_2OH	OH	H	CH_3
epi-pterosin L:	CH_2OH	CH_3	OH	H	CH_3

	R_1	R_2	R_3
IV:	CH_3	CH_3	OH
VII:	COOH	CH_3	OH
VIII:	CH_3	CH_2OH	OH
IX:	CH_3	OH	CH_2OH



V



VI

Fig. 1

I were found at $\delta_{Pyr.-d_5}$ 67.0 and 19.1, respectively. These chemical shift values are close to those of the α-hydroxymethyl group and β-methyl group at C-2 in pterosin L (δ 67.1 and 19.4), rather than to those of the β-hydroxymethyl group and α-methyl group at C-2 in *epi*-pterosin L (δ 66.0 and 16.6). Accordingly, the hydroxymethyl group at C-2 is concluded to be oriented in the α-configuration. The absolute configuration of C-3 in I was established as *R* from the circular dichroism Cotton effect, $[\theta]_{330}$ +11400 (MeOH).[10] From these results, I was concluded to be (2*R*,3*R*)-3-hydroxy-6-(2-hydroxyethyl)-2,7-bishydroxymethyl-2,5-dimethyl indan-1-one.

(2) *Dicksonia gigantea* KARST.

From this fern, *trans*-cinnamic acid (X), onitin (XI),[11] pterosin D (XII)[10] and isoquercitrin (XIII) were isolated.

(3) *Paesia anfractuosa* C. CHR.

From this fern, kaempferol-3-*O*-rutinoside (XIV) and rutin (XV) were isolated.

Experimental

The instruments used to obtain physical data, the materials and the experimental conditions were the same as those described in part XXXVII[2] in this series unless otherwise specified.

Isolation Procedure——1) *Jamesonia scammanae* A. TRYON: The ferns were collected in Costa Rica in April. The air-dried ferns (100 g) were extracted 3 times with methanol (500 ml) under reflux for 6 h. The combined extracts (1.5 l) were passed through an activated charcoal (10 g) column of 3 cm diameter and the column was further eluted with methanol (3 l). The combined solution (4.5 l) was concentrated *in vacuo* to 200 ml and partitioned between $CHCl_3$ (200 ml) and H_2O (150 ml). The lower layer was concentrated *in vacuo* to a syrup (6 g). The syrup was chromatographed on silica gel (50 g) with $CHCl_3$ (Frac. 1), 3% MeOH in $CHCl_3$ (Frac. 2), 5% MeOH in $CHCl_3$ (Frac. 3) and 7% MeOH in $CHCl_3$ (Frac. 4) as eluents. Frac. 1 was chromatographed on silica gel with 50% $CHCl_3$ in *n*-hexane to yield compound IV (20 mg) and a mixture of compound V and VI which was rechromatographed on silica gel impregnated with $AgNO_3$. Elution with $CHCl_3$ gave compounds V (40 mg) and VI (23 mg) in a pure form. From frac. 2, compound VII (50 mg) was obtained. Frac. 3 was chromatographed on silica gel (50 g) with 2% MeOH in $CHCl_3$, followed by chromatography on silica gel with 15% ethyl acetate in $CHCl_3$ to yield compounds VIII (10 mg) and IX (15 mg). Frac. 4 was chromatographed on alumina with 1% MeOH in $CHCl_3$, followed by preparative layer chromatography (PLC) (solvent system, $CHCl_3$–ether, 1 : 1) to yield pterosin B (III, 5 mg). The upper layer was concentrated *in vacuo* to a syrup (2 g), which was subjected to DCCC ($CHCl_3$–MeOH–H_2O, 4 : 4 : 3). Frac. 75—89 was chromatographed on alumina with 15% MeOH in $CHCl_3$, followed by PLC (solvent system, $CHCl_3$–MeOH, 10 : 1) to yield jamesonin (I, 8 mg). Frac. 90—115 was chromatographed on silica gel with 5% MeOH in $CHCl_3$ to give pterosin S (II, 30 mg).

2) *Dicksonia gigantea* KARST.: The ferns were collected in Costa Rica in April. The air-dried ferns (300 g) were extracted 3 times with MeOH (1 l) under reflux for 6 h. The combined extracts (3 l) were passed through an activated

charcoal (35 g) column of 5 cm diameter and the column was further eluted with MeOH (5 l). The combined solution (8 l) was concentrated *in vacuo* to 200 ml and partitioned between $CHCl_3$ (600 ml) and H_2O (600 ml). The lower layer was concentrated *in vacuo* to a syrup (4.9 g), which was chromatographed on silica gel (55 g) with 1% MeOH in $CHCl_3$ (Frac. 1) and 2% MeOH in $CHCl_3$ (Frac. 2). Frac. 1 was subjected to PLC (solvent system, $CHCl_3$–MeOH, 10 : 1) to yield *trans*-cinnamic acid (X, 15 mg). Frac. 2 was subjected to PLC (solvent system, $CHCl_3$–ether, 1 : 3) to yield onitin (XI, 45 mg) and pterosin D (XII, 13 mg). The upper layer was subjected to DCCC ($CHCl_3$–MeOH–H_2O, 4 : 4 : 3), followed by chromatography on polyamide with MeOH to yield isoquercitrin (XIII, 40 mg).

3) *Paesia anfractuosa* C. CHR.: The ferns were collected in Costa Rica in April. The air-dried ferns (120 g) were extracted 3 times with MeOH (600 ml) under reflux for 6 h. The combined extracts (1.8 l) were passed through an activated charcoal (12 g) column of 3 cm diameter and the column was further eluted with MeOH (3 l). The combined solution (4.8 l) was concentrated *in vacuo* to 70 ml and partitioned between $CHCl_3$ (200 ml) and H_2O (200 ml). The upper layer was subjected to DCCC($CHCl_3$–MeOH–H_2O, 4 : 4 : 3), followed by chromatography on polyamide with MeOH to give compound XIV (100 mg) and rutin (XV, 20 mg).

Jamesonin (I)——Colorless amorphous powder, $[\alpha]_D^{24}$ +9.6° (c=0.35, MeOH), circular dichroism (CD) $[\theta]_{330}^{30}$ +11400 (MeOH), UV λ_{max}^{MeOH} nm (log ε): 218 (4.31), 261.5 (3.91), 304 (3.23). Infrared (IR) ν_{max}^{KBr} cm^{-1}: 3320, 2930, 1700, 1600, 1460, 1040. ^{1}H-NMR (in Pyr.-d_5) δ: 1.33 (3H, s), 2.38 (3H, s), 3.32 (2H, t, J=7 Hz), 4.05 (2H, t, J=7 Hz), 4.18 (2H, AB quartet, J=10 Hz), 5.13 (1H, s), 5.46 (2H, AB quartet, J=12 Hz), 7.59 (1H, s). ^{13}C-NMR (in Pyr.-d_5) δ: 208.4 (C-1), 56.7 (C-2), 77.1 (C-3), 127.1 (C-4), 145.6 (C-5), 138.8 (C-6), 139.9 (C-7), 132.3 (C-8), 154.8 (C-9), 67.0 (C-10), 19.1 (C-11), 21.3 (C-12), 32.7 (C-13), 61.6 (C-14), 56.3 (C-15). Mass spectra (MS) m/z: 262 ($M^+ - H_2O$, 50%), 231 ($M^+ - H_2O - CH_2OH$, 86%), 213 ($M^+ - 2\times H_2O - CH_2OH$, 100%), Calcd for $C_{15}H_{18}O_4$: 262.1203 ($M - H_2O$), Found: 262.1200 ($M^+ - H_2O$).

Pterosin S (II)——Colorless needles from a mixture of acetone and *n*-hexane, mp 125—127 °C, $[\alpha]_D^{23}$ +60.0° (c=0.30, MeOH). UV λ_{max}^{MeOH} nm (log ε): 216.5 (4.58), 259 (4.12), 301 (3.47). IR ν_{max}^{KBr} cm^{-1}: 3300, 1705, 1680, 1600, 1480, 1450, 1345, 1220, 920. ^{1}H-NMR (60 MHz, in CD_3OD) δ: 1.30 (3H, d, J=8 Hz), 2.46 (3H, s), 2.30—2.50 (1H, m, overlapping with δ 2.46), 3.05 (2H, t, J=7 Hz), 3.65 (2H, t, J=7 Hz), 4.65 (1H, d, overlapping with $CH_3O\underline{H}$), 4.99 (2H, br s), 7.40 (1H, s). ^{13}C-NMR (in Pyr.-d_5) δ: 205.8 (C-1), 54.4 (C-2), 74.9 (C-3), 126.9 (C-4), 145.4 (C-5), 138.3 (C-6), 139.3 (C-7), 131.5 (C-8), 154.4 (C-9), 13.0 (C-11), 21.2 (C-12), 32.3 (C-13), 61.6 (C-14), 56.2 (C-15). MS m/z: 250 (M^+), 232, 221, 205, 203, 202. This product was identical with an authentic sample on direct comparison (thin-layer chromatography (TLC), IR, ^{1}H-NMR, ^{13}C-NMR and mixed fusion).

Pterosin B (III)——Colorless syrup, $[\alpha]_D^{24}$ +26.7° (c=0.45, $CHCl_3$), UV λ_{max}^{MeOH} nm (log ε): 216 (4.55), 260 (4.18), 303 (3.40). ^{1}H-NMR (in $CDCl_3$) δ: 1.27 (3H, d, J=8 Hz), 2.43 (3H, s), 2.67 (3H, s), 3.01 (2H, t, J=7 Hz), 3.75 (2H, t, J=7 Hz), 7.05 (1H, s). MS m/z: 218 (M^+), 203, 187, 175, 149, 115. This product was identical with an authentic sample on direct comparison (TLC, ^{1}H-NMR and MS).

16α-Hydroxy-*ent*-kaurane (IV)——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 217—218 °C, $[\alpha]_D^{24}$ −57.5° (c=0.56, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3320, 2940, 2920, 2860, 2840, 1460, 1365, 1115. ^{1}H-NMR (in Pyr.-d_5) δ: 0.78 (3H, s), 0.83 (3H, s), 0.98 (3H, s), 1.55 (3H, s). ^{13}C-NMR (in Pyr.-d_5) δ: 40.5 (C-1), 18.9 (C-2), 42.3* (C-3), 33.3 (C-4), 56.2 (C-5), 20.7 (C-6), 42.4* (C-7), 45.5 (C-8), 57.2 (C-9), 39.5 (C-10), 18.4 (C-11), 27.3 (C-12), 49.3 (C-13), 38.0 (C-14), 58.7 (C-15), 77.8 (C-16), 25.0 (C-17), 33.7 (C-18), 21.7 (C-19), 18.0 (C-20). *) Assignments of chemical shifts may be reversed. MS m/z: 290 (M^+), 272, 257, 232, 229, 217, Calcd for $C_{20}H_{34}O_1$: 290.2608 (M), Found: 290.2608 (M^+).

***ent*-Kaur-16-en-19-oic Acid (V)**——Colorless needles from a mixture of MeOH and H_2O, mp 168—170 °C, $[\alpha]_D^{27}$ −112.4° (c=0.77, $CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3060, 2920, 2850, 1690, 1650, 1460, 1265, 1180, 870. ^{1}H-NMR (in Pyr.-d_5) δ: 1.12 (3H, s), 1.33 (3H, s), 4.85 (2H, br d, J=2 Hz). ^{13}C-NMR (in Pyr.-d_5) δ: 41.1 (C-1), 19.8 (C-2), 38.7 (C-3), 43.8 (C-4), 57.1 (C-5), 22.5 (C-6), 41.6 (C-7), 44.4 (C-8), 55.2 (C-9), 39.9 (C-10), 18.7 (C-11), 33.7 (C-12), 44.2 (C-13), 39.9 (C-14), 49.3 (C-15), 155.7 (C-16), 103.4 (C-17), 29.4 (C-18), 179.8 (C-19), 16.0 (C-20). MS m/z: 302 (M^+), 287, 259, 243, 241, 213, Calcd for $C_{20}H_{30}O_2$: 302.2245 (M), Found: 302.2247 (M^+).

***ent*-Kaur-15-en-19-oic Acid (VI)**——Colorless needles from a mixture of MeOH and H_2O, mp 189—190 °C, $[\alpha]_D^{24}$ −46.4° (c=1.82, $CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3020, 2940, 2920, 2850, 1690, 1650, 1470, 1450, 1270, 950, 810. ^{1}H-NMR (in Pyr.-d_5) δ: 1.18 (3H, s), 1.35 (3H, s), 1.69 (3H, d, J=2 Hz), 5.12 (1H, br s). ^{13}C-NMR (in Pyr.-d_5) δ: 41.2 (C-1), 19.8 (C-2), 38.7 (C-3), 44.2 (C-4), 56.9 (C-5), 21.5 (C-6), 44.2 (C-7), 49.6 (C-8), 48.3 (C-9), 40.2 (C-10), 19.2 (C-11), 25.1 (C-12), 45.0 (C-13), 39.9 (C-14), 135.7 (C-15), 142.1 (C-16), 15.5 (C-17), 29.4 (C-18), 179.9 (C-19), 15.9 (C-20). MS m/z: 302 (M^+), 287, 259, 241, 193, 187, Calcd for $C_{20}H_{30}O_2$: 302.2245 (M), Found: 302.2241 (M^+).

16α-Hydroxy-*ent*-kauran-19-oic Acid (VII)——Colorless needles from acetone, mp 283—285 °C, $[\alpha]_D^{22}$ −92.0° (c=1.28, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3450, 2920, 2850, 1690, 1460, 1440, 1370, 1250, 1160, 930, 870. ^{1}H-NMR (in Pyr.-d_5) δ: 1.18 (3H, s), 1.33 (3H, s), 1.54 (3H, s). ^{13}C-NMR (in Pyr.-d_5) δ: 41.0 (C-1), 19.7 (C-2), 38.6 (C-3), 43.8 (C-4), 56.3 (C-5), 22.8 (C-6), 42.6 (C-7), 45.4 (C-8), 57.0 (C-9), 39.9 (C-10), 18.6 (C-11), 27.2 (C-12), 49.0 (C-13), 37.9 (C-14), 58.4 (C-15), 77.9 (C-16), 25.0 (C-17), 29.3 (C-18), 179.8 (C-19), 16.0 (C-20). MS m/z: 320 (M^+), 302, 287, 262, 247, 217, 187, Calcd for $C_{20}H_{32}O_3$: 320.2336 (M), Found: 320.2334 (M^+).

16α,17-Dihydroxy-*ent*-kaurane (VIII)——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 187—188 °C (dec.). $[\alpha]_D^{17}$ −49.5° (c=0.36, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 2930, 2870, 2840, 1450, 1390, 1370, 1070, 1030,

880. ^{1}H-NMR (in Pyr.-d_5) δ: 0.79 (3H, s), 0.83 (3H, s), 0.98 (3H, s), 4.08 (2H, br s). ^{13}C-NMR (in Pyr.-d_5) δ: 40.4 (C-1), 18.7* (C-2), 42.2 (C-3), 33.3 (C-4), 56.2 (C-5), 20.7 (C-6), 42.5 (C-7), 44.9 (C-8), 57.1 (C-9), 39.5 (C-10), 18.8* (C-11), 26.8 (C-12), 46.0 (C-13), 37.8 (C-14), 54.0 (C-15), 81.5 (C-16), 66.5 (C-17), 33.6 (C-18), 21.7 (C-19), 18.0 (C-20). *) Assignments of chemical shifts may be reversed. MS *m/z*: 306 (M^+), 288, 275, 257, 232, Calcd for $C_{20}H_{34}O_2$: 306.2562 (M), Found: 306.2561 (M^+).

16β,17-Dihydroxy-*ent*-kaurane (IX)——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 176—177 °C (dec.), $[\alpha]_D^{24}$ −49.3° (*c*=0.52, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3370, 2920, 2860, 2840, 1460, 1385, 1370, 1270, 1110, 1030, 800. ^{1}H-NMR (in Pyr.-d_5) δ: 0.80 (3H, s), 0.84 (3H, s), 1.02 (3H, s), 3.74 (1H, d, *J*=11 Hz), 3.86 (1H, d, *J*=11 Hz). ^{13}C-NMR (in Pyr.-d_5) δ: 40.6 (C-1), 19.2 (C-2), 42.3 (C-3), 33.3 (C-4), 56.2 (C-5), 20.4 (C-6), 42.3 (C-7), 43.9 (C-8), 57.6 (C-9), 39.6 (C-10), 18.0 (C-11), 27.7 (C-12), 41.9 (C-13), 38.7 (C-14), 53.6 (C-15), 79.7 (C-16), 70.5 (C-17), 33.7 (C-18), 21.8 (C-19), 17.8 (C-20). MS *m/z*: 306 (M^+), 288, 275, 257, Calcd for $C_{20}H_{34}O_2$: 306.2556 (M), Found: 306.2556 (M^+).

***trans*-Cinnamic Acid (X)**——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 132—133 °C, UV λ_{max}^{MeOH} nm (log ε): 216 (4.12), 220 (4.03), 272 (4.15). IR ν_{max}^{KBr} cm^{-1}: 2900, 1670, 1625, 1600, 1575, 1495, 1450, 975, 765, 705. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 6.40 (1H, d, *J*=16 Hz), 7.25—7.55 (5H, m), 7.63 (1H, d, *J*=16 Hz). This product was identical with an authentic sample on direct comparison (IR and mixed fusion).

Onitin (XI)——Colorless needles from $CHCl_3$, mp 212—213 °C, UV λ_{max}^{MeOH} nm (log ε): 232 (4.51), 270.5 (4.15), 324 (3.71). IR ν_{max}^{KBr} cm^{-1}: 3380, 1680, 1585, 1460, 1380, 1125, 1005, 930, 860. ^{1}H-NMR (in CD_3OD) δ: 1.25 (6H, s), 2.31 (3H, s), 2.56 (3H, s), 2.80 (2H, s), 2.97 (2H, t, *J*=8 Hz), 3.58 (2H, t, *J*=8 Hz). MS *m/z*: 248 (M^+), 233, 217, 205. This product was identical with an authentic sample on direct comparison (IR, ^{1}H-NMR and mixed fusion).

Pterosin D (XII)——Colorless needles from a mixture of $CHCl_3$ and MeOH, mp 190—191 °C, $[\alpha]_D^{20}$ +5.8° (*c*=0.5, EtOH). UV λ_{max}^{MeOH} nm (log ε): 216 (4.58), 259 (4.28), 303 (3.28). IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 1710, 1702, 1600, 1460, 1380, 1060, 990. ^{1}H-NMR (in CD_3OD) δ: 1.03 (3H, s), 1.17 (3H, s), 2.47 (3H, s), 2.63 (3H, s), 2.99 (2H, t, *J*=8 Hz), 3.61 (2H, t, *J*=8 Hz), 4.71 (1H, s), 7.30 (1H, s). MS *m/z*: 248 (M^+), 233, 217, 199. This product was identical with an authentic sample on direct comparison (IR, ^{1}H-NMR and mixed fusion).

Isoquercitrin (XIII)——Yellow needles from a mixture of MeOH and H_2O, mp 234—236 °C, $[\alpha]_D^{20}$ −72.1° (*c*=1.00, MeOH). UV λ_{max}^{MeOH} nm (log ε): 258 (4.23), 360 (4.18). IR ν_{max}^{KBr} cm^{-1}: 3250, 1670, 1610, 1500, 1365, 1310, 1205, 1060, 1015, 800. ^{1}H-NMR (in DMSO-d_6) δ: 5.48 (1H, d, *J*=7 Hz), 6.21 (1H, d, *J*=2 Hz), 6.42 (1H, d, *J*=2 Hz), 6.85 (1H, d, *J*=9 Hz), 7.48—7.68 (2H, m). XIII was hydrolyzed with 3% aq HCl to give quercetin and D-glucose. This product was identical with an authentic sample on direct comparison (IR, ^{1}H-NMR and mixed fusion).

Kaempferol-3-*O*-rutinoside (XIV)——Yellow needles from a mixture of MeOH and H_2O, mp 186—187 °C, $[\alpha]_D^{20}$ +4.2° (*c*=0.67, MeOH). UV λ_{max}^{MeOH} nm (log ε): 268 (4.32), 352 (4.24). IR ν_{max}^{KBr} cm^{-1}: 3400, 1655, 1615, 1565, 1510, 1450, 1365, 1180, 830. ^{1}H-NMR (in DMSO-d_6) δ: 1.03 (3H, d, *J*=6 Hz), 5.14 (1H, br s), 5.33 (1H, d, *J*=7 Hz), 6.22 (1H, br s), 6.42 (1H, br s), 6.89 (2H, d, *J*=9 Hz), 7.98 (2H, d, *J*=9 Hz). ^{13}C-NMR (in DMSO-d_6) δ: 156.8* (C-2), 133.2 (C-3), 177.3 (C-4), 161.1 (C-5), 98.7 (C-6), 164.0 (C-7), 93.8 (C-8), 156.4* (C-9), 103.9 (C-10), 120.8 (C-1′), 130.8 (C-2′), 115.1 (C-3′), 159.8 (C-4′), 115.1 (C-5′), 130.8 (C-6′), 101.3 (C-1″), 74.2 (C-2″), 76.3 (C-3″), 69.9 (C-4″), 75.7 (C-5″), 66.9 (C-6″), 100.7 (C-1‴), 70.3 (C-2‴), 70.6 (C-3‴), 71.8 (C-4‴), 68.2 (C-5‴), 17.7 (C-6‴). *) Assignments of chemical shifts may be reversed. XIV was hydrolyzed with 5% aq HCl to yield kaempferol, D-glucose and L-rhamnose. This product was identical with an authentic sample on direct comparison (IR, ^{13}C-NMR and mixed fusion).

Rutin (XV)——Yellow needles from a mixture of MeOH and H_2O, mp 187—188 °C, $[\alpha]_D^{20}$ +13.0° (*c*=0.5, EtOH), UV λ_{max}^{MeOH} nm (log ε): 259 (4.37), 270 (4.31) sh, 360 (4.26). IR ν_{max}^{KBr} cm^{-1}: 3300, 2910, 1650, 1600, 1500, 1450, 1360, 1290. ^{1}H-NMR (in DMSO-d_6) δ: 1.01 (3H, d, *J*=6 Hz), 5.12 (1H, br s), 5.32 (1H, d, *J*=7 Hz), 6.18 (1H, d, *J*=2 Hz), 6.38 (1H, d, *J*=2 Hz), 6.83 (1H, d, *J*=9 Hz), 7.42—7.58 (2H, m). ^{13}C-NMR (in DMSO-d_6) δ: 156.5* (C-2), 133.1 (C-3), 177.1 (C-4), 161.0 (C-5), 98.5 (C-6), 163.9 (C-7), 93.5 (C-8), 156.2* (C-9), 103.8 (C-10), 121.0 (C-1′), 115.1 (C-2′), 144.5 (C-3′), 148.2 (C-4′), 116.1 (C-5′), 121.4 (C-6′), 101.0 (C-1″), 73.9 (C-2″), 76.3 (C-3″), 69.9 (C-4″), 75.7 (C-5″), 66.9 (C-6″), 100.6 (C-1‴), 70.2 (C-2‴), 70.4 (C-3‴), 71.7 (C-4‴), 68.1 (C-5‴), 17.6 (C-6‴). *) Assignments of chemical shifts may be reversed. This product was identical with an authentic sample on direct comparison (IR, ^{13}C-NMR and mixed fusion).

References and Notes

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