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TWO PRENYLFLAVANONES FROM *EUCHRESTA JAPONICA**

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Key Word Index—*Euchresta japonica*; Leguminosae; euchrestaflavanone B; euchrestaflavanone C; 5, 7, 4′-trihydroxy-6, 8-diprenylisoflavone; warangalone; osajin; prenylflavonoids.

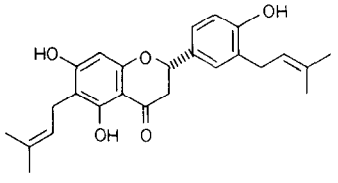
Abstract—Two new prenylflavanones, named euchrestaflavanone B and C were isolated from the roots of *Euchresta japonica*. Their structures have been confirmed by spectroscopic and chemical evidence, respectively.

INTRODUCTION

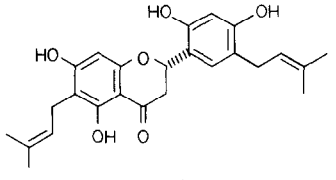
Previously we reported the isolation and the structural elucidation of euchrestaflavanone A from the roots of *Euchresta japonica* Hook. f. ex Regel which have been used as a substitute for a Chinese drug, Shan-Dou-Gen [1]. In our further studies on this drug, two new prenylflavanones, euchrestaflavanone B (**1**) and C (**2**), together with 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**3**), warangalone (**4**) and osajin (**5**) have been isolated. This paper deals with the isolation and structural determination of these compounds.

RESULTS AND DISCUSSION

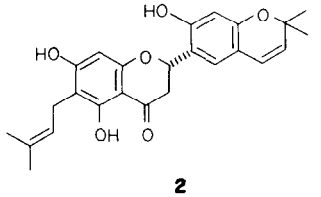
Euchrestaflavanone B (**1**) (M^+ 424, $[\alpha]_D^{22} - 31.0°$ in EtOH, $C_{25}H_{28}O_6$) was isolated as colorless needles, mp 188–190° from the ether-soluble fraction of the methanol extract of the roots of *E. japonica*. It gave a greenish-brown color in the ferric chloride test, a dark blue color in the Gibbs test and a positive magnesium–hydrochloric acid test. The IR spectrum of **1** showed strong absorptions at 1630 cm^{-1} (chelated C=O) and 3400 cm^{-1} (OH). The UV spectrum (λ_{max}^{EtOH} 294, 334(sh) nm) suggested a flavanone structure. It formed a tetra-acetate (**1a**) indicating the presence of



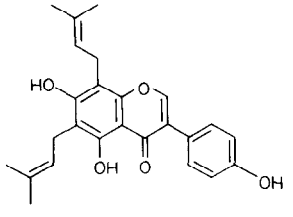
Euchrestaflavanone A



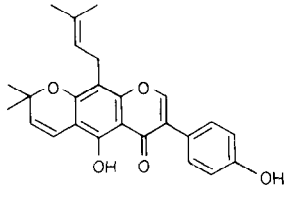
1
Euchrestaflavanone B



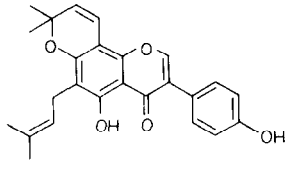
2
Euchrestaflavanone C



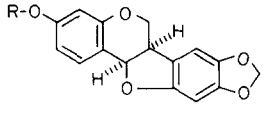
3
5,7,4′-Trihydroxy-6,8-diprenylisoflavone



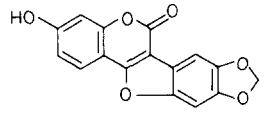
4
Warangalone (scandenone)



5
Osajin



ℓ-Maackiain R=H
Trifolirhizin R= glucose



Medicagol

*Part 17 in the series "Studies on the Constituents of *Sophora* Species". For Part 16 see ref. [1].

four hydroxyl groups. The ^{1}H NMR spectrum of **1** (CD_3COCD_3) showed δ 5.68 (1H, *dd*, J = 11.8 and 3.7 Hz) and 2.6–3.2 (2H, *m*), attributed to the C-ring protons (H-2, H_2-3) of the flavanone. It also indicated the presence of two 3,3-dimethylallyl groups [δ 1.63, 1.71 (12 H, each *s*, $Me_2 \times 2$), 3.25 (4 H, *br d*, J = 7.5 Hz, Ar–CH_2–CH= $\times 2$), 5.24, 5.33 (each 1 H, each *br t*, J = 7.5 Hz, $-CH_2-CH=C\langle \times 2$)], four hydroxyl groups [δ 8.3 (2 H, *br s*), 9.6 (1 H, *br s*) and 12.2 (1H, *s*, chelated with C-4 carbonyl); both of which disappeared on the addition of D_2O] and three aromatic protons [δ 6.03 (1 H, *s*, H-6 or H-8), 6.50 (1 H, *s*, H-3'), 7.23 (1 H, *s*, H-6')].

The mass spectrum of **1** showed major ion peaks at *m/z* (rel. int.) 406 (100), 351 (25.2), 220 (3.9) and 204 (1.5). The ion peaks at *m/z* 220 and 204 were derived from a retro-Diels–Alder fragmentation. In view of the ^{1}H NMR spectral data, the ion peak at *m/z* 220 must include the A-ring. This ion loses C_4H_7 to yield the ion peak at *m/z* 165 (57.9) and therefore the A-ring contains one 3,3-dimethylallyl group. On the other hand, the ion peak at *m/z* 204 arises from the B-ring and loses C_4H_7 to yield the ion peak at *m/z* 149 (14.5). Therefore the B-ring also contains one 3,3-dimethylallyl group. From these data, it is clear that there are two 3,3-dimethylallyl groups in **1**, one being attached to the A-ring and the other to the B-ring (Scheme 1).

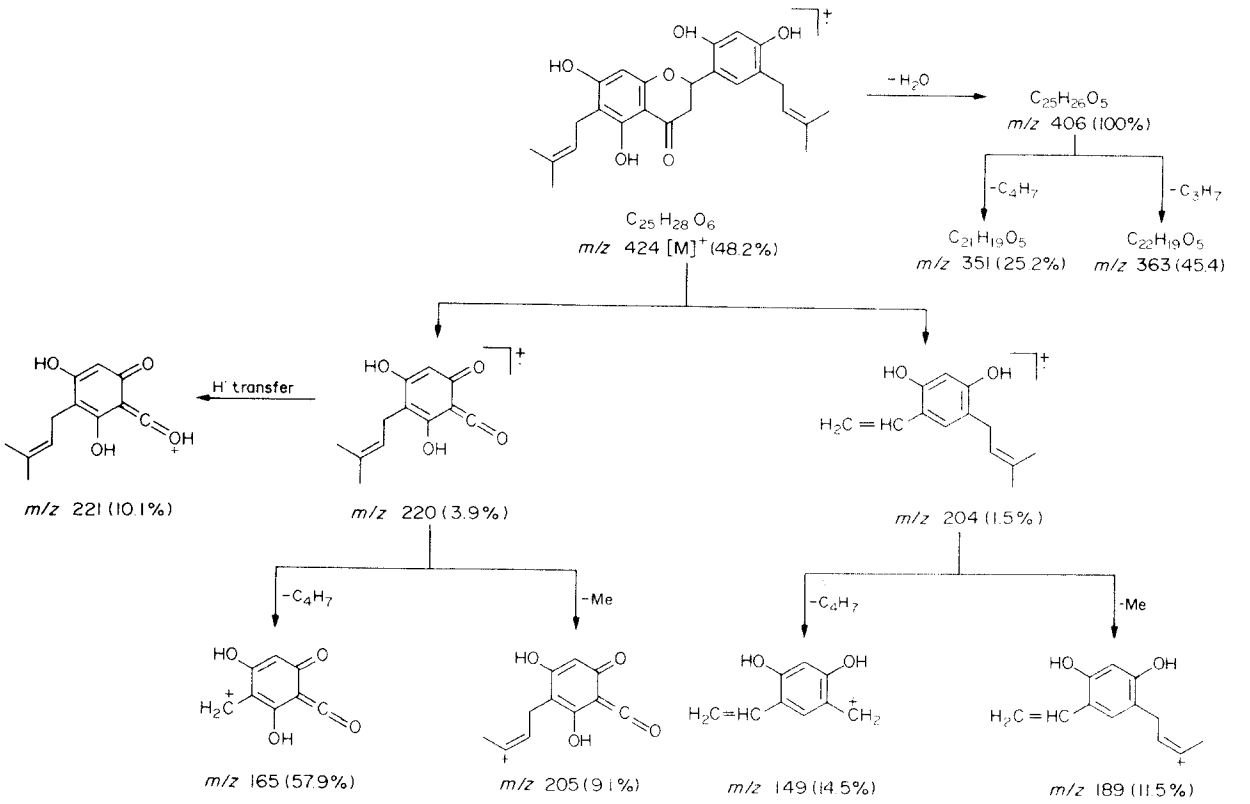
Since the ^{13}C NMR spectrum of **1** showed signals at δ 74.1 (*d*) and 41.6(*t*), attributed to C-2 and C-3 of flavanones, **1** was determined to be a flavanone derivative. The signals of δ 106.9 (C-6) and 95.1 (C-8) are the same as those of euchrestaflavanone A [1], and the 3,3-dimethylallyl group (A-ring) was shown to be located at C-6 (Fig. 1), which was also supported by a positive Gibbs test.

UV shifts after the addition of sodium acetate, aluminium chloride or NaOEt showed that the three hydroxyl groups were located at C-7, C-5 and C-4'. Since the ^{1}H NMR spectrum (B-ring) of **1** showed two singlet proton signals of the aromatic ring, the 3,3-dimethylallyl group in the B-ring must be located at C-3' and the fourth hydroxyl group at C-2'. This was supported by the following acid-catalysed cyclization of **1**.

On refluxing a solution of **1** in methanol–hydrochoric acid, the 3,3-dimethylallyl side chain cyclized with the neighboring hydroxyl group to afford only one chromane (**1b**; dicycloeuchrestaflavanone B). **1b** has the composition $C_{25}H_{28}O_6$, and gave a ^{1}H NMR spectrum ($CDCl_3$) showing the presence of four tertiary methyl groups at δ 1.33 (12 H, *s*) and four methylene groups of a 2,2-dimethylchromane ring at δ 1.79 (4H, *br t*, J = 7.1 Hz), 2.63 (2H, *t*, J = 7.1 Hz) and 2.71 (2 H, *t*, J = 7.1 Hz). It also showed two hydroxyl protons at δ 5.9 (1 H, *s*, OH-2') and 12.4 (1 H, *s*, OH-5), both of which disappeared on the addition of D_2O. Accordingly, the cyclized product could be formulated as **1b**.

From these data, the structure of **1** was concluded to be 5,7,2',4'-tetrahydroxy-6, 5'-di-(3,3-dimethylallyl)-flavanone.

The absolute configuration of **1** was determined as (−)-2*S*-flavanone by the CD spectra [2]. Since the 2-aryl group in **1** is equatorial ($J_{2,3ax}$ = 11.8 Hz) [3] the



Scheme 1. Mass spectral fragmentation of **1**.

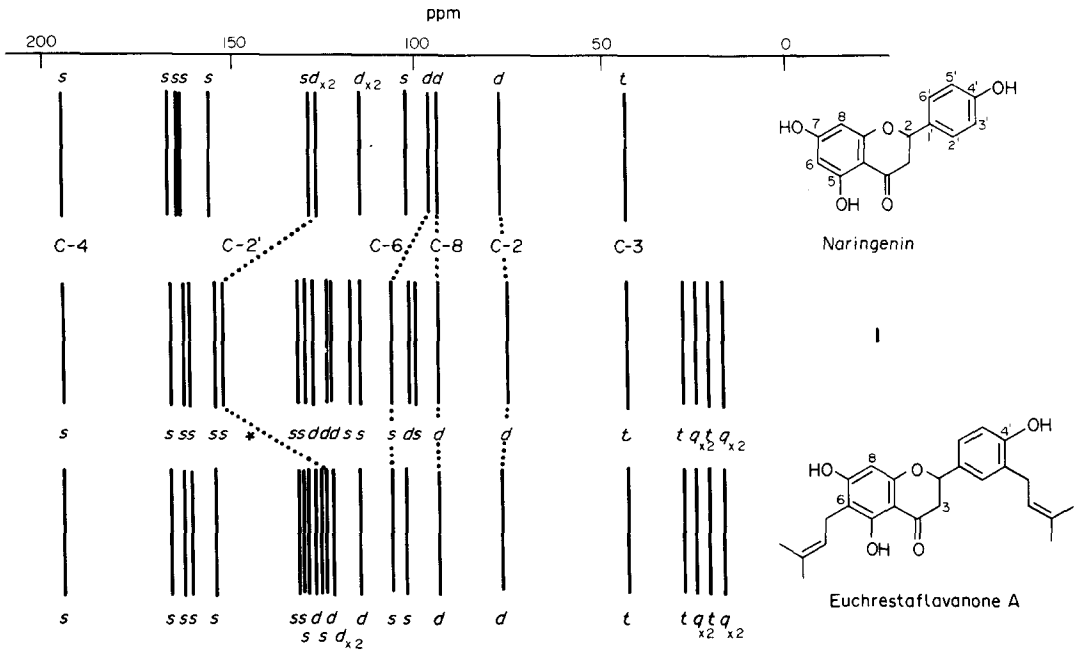


Fig. 1. ^{13}C NMR spectrum of **1** (in DMSO-d_6). Off-resonance decoupling (SFORD). *s*, Singlet; *d*, doublet; *t*, triplet; *q*, quartet.* The position of C-2' in **1** corresponds to C-6' of euchrestaflavanone A.

positive Cotton effect at 339 nm ($\Delta\epsilon - 0.14$) and the negative Cotton effect at 295 nm ($\Delta\epsilon - 3.01$) allows the assignment of the *S*-configuration at C-2 in **1**.

Euchrestaflavanone C (**2**) (M^+ 422, $[\alpha]_D^{22} - 103.1°$ in ethanol, $C_{25}H_{26}O_6$) was obtained as pale yellow needles, mp 198–200°. It gave a greenish-brown color in the ferric chloride test, a blue color in the Gibbs test and a positive magnesium–hydrochloric acid test. The IR spectrum of **2** showed a strong absorptions at 1640 cm^{-1} (chelated C=O) and 3350 cm^{-1} (OH). The UV spectrum (λ_{max}^{EtOH} = 293, 342(sh) nm) suggested a flavanone structure. It formed a triacetate (**2a**) indicating the presence of three hydroxyl groups. The ^1H NMR spectrum of **2** (CD_3COCD_3) showed δ 5.68 (1 H, *dd*, J = 11.6 and 3.8 Hz) and 2.6–3.2 (2 H, *m*), attributed to the C-ring protons (H-2, H_2-3) of the flavanone. It also indicated the presence of one 3,3-dimethylallyl group [δ 1.63 (6 H, *s*, Me × 2), 3.25 (2 H, *br d*, J = 7.4 Hz, Ar–C$\underline{H}_2$–CH=), 5.22 (1 H, *br t*, J = 7.4 Hz, –CH_2–C$\underline{H}$=C<), one 2,2-dimethylchromene ring [δ 1.40 (6 H, *s*, Me × 2), 5.61 (1 H, *d*, J = 10.0 Hz), 6.36 (1 H, *d*, J = 10.0 Hz)], three hydroxyl groups [δ 9.0 (2 H, *br s*) and 12.2 (1 H, *s*, chelated with C-4 carbonyl); both of which disappeared on the addition of D_2O] and three aromatic protons [δ 6.04 (1 H, *s*, H-6 or H-8), 6.38 (1 H, *s*, H-3'), 7.22 (1 H, *s*, H-6')].

The mass spectrum of **2** showed major ion peaks at *m/z* 407 (17.6), 404 (32.9), 389 (6.9), 220 (4.0) and 202 (0.7). The ion peaks at *m/z* 220 and 202 were derived from a retro-Diels–Alder fragmentation. In view of the ^1H NMR spectral data, the ion peak at *m/z* 220 must include the A-ring. This ion loses C_4H_7 to yield the ion peak at *m/z* 165 (46.8) and therefore the A-ring contains one 3,3-dimethylallyl group. On the other hand, the ion peak at *m/z* 202 arises from the B-ring. It loses Me to yield the ion peak at *m/z* 187 (100). Therefore the B-ring contains one 2,2-dimethylchromene ring. Since the ^{13}C NMR spectrum of **2** showed signals at δ 106.9 (C-6) and 95.3 (C-8) which are the same as those of **1**, the 3,3-dimethylallyl group was shown to be located at C-6. The substitution pattern of B-ring was determined to be 2',4'-dihydroxy-5'-C-substituted by comparison of the chemical shifts of **1** and **2** (Table 1).

From these spectral data and biogenetic considerations, the structure of euchrestaflavanone C (**2**) was concluded to be 5,7,2'-trihydroxy-6-(3,3-dimethylallyl) - 2",2" - dimethylpyrano - (5",6" : 4',5') - flavanone. The absolute configuration of **2** was determined as (−)-2*S*-flavanone by the CD spectra as well as **1**.

Other compounds (**3–5**) are referred to in the Experimental.

Table 1. ^{13}C NMR spectral data of **1** and **2** (B-ring, in DMSO-d_6)

Compound	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
1	118.1	153.2	102.3	155.5	115.5	127.3
2	117.6	153.5	102.9	155.5	112.8	127.7

EXPERIMENTAL

All mps were uncorr. ^{1}H NMR spectra were run at 100 MHz using TMS as int. standard. ^{13}C NMR spectra were run at 25.1 MHz using the FT mode and TMS as int. standard. MS were recorded at 70 eV with a direct inlet system. HPLC were carried out with solvent MeOH–H_2O (4 : 1) using a μ-Bondapak C 18 (Waters Ltd., 3.9 mm × 30 cm) column employing a monitoring flow system ($UV_{254\,nm}$) coupled to a recorder at a flow rate of 2.0 ml/min. TLC was conducted on Si gel and solvent systems were n-C_6H_{14}–Me_2CO (2 : 1) and C_6H_6–Me_2CO (5 : 2).

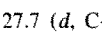
Plant material. The dried roots of *Euchresta japonica* Hook. f. ex Regel, which were collected in Mt. Ichifusa, Kumamoto prefecture, Japan in April 1981.

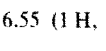
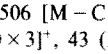
Isolation of compounds. Cut roots (1.2 kg) were extracted × 3 with boiling MeOH (30 l.) and the solvent removed *in vacuo*. The extract (360 g) was shaken with Et_2O and H_2O. The Et_2O extract was concd (73 g) and chromatographed on Si gel using C_6H_6 and C_6H_6–EtOAc (9 : 1–1 : 1) as solvents to give (−)-maackiain (136 mg), sitosterol (184 mg), euchrestaflavanone A (1.2 g), medicagol (24 mg) and crude **1–5**. Crude **1–5** were subjected to rechromatography on Si gel by using n-C_6H_{14} and n-C_6H_{14}–Me_2CO (9 : 1–1 : 1) as eluents and each fraction was checked by TLC to yield **1** (87 mg), **2** (62 mg), **3** (640 mg), **4** (32 mg) and **5** (32 mg), respectively.

Euchrestaflavanone B (**1**). Colorless needles (from dilute MeOH), mp 188–190°, $[\alpha]_D^{22}$ − 31.0° (EtOH; *c* 1.0). Found: M^+ 424.1886; $C_{25}H_{28}O_6$ requires 424.1895. HPLC R_t: 4.5 min. UV λ_{max}^{EtOH} nm (log ϵ): 294 (3.78), 334 sh (2.97); + NaOAc: 284 (4.27), 338 (4.10); + $AlCl_3$: 225 sh (4.41), 314 (3.83); + NaOEt: 250 sh (4.40), 332 (4.05). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1630 (C=O), 1610, 1510 (arom. C=C). ^{13}C NMR (DMSO-d_6): δ 17.6 (*q*, Me × 2, A,B-ring), 21.3 (*t*, –CH$_2$–CH=C<, A-ring), 25.5 (*q*, Me × 2, A,B-ring), 27.5 (*t*, –CH$_2$–CH=C<, B-ring), 41.6 (*t*, C-3), 74.1 (*d*, C-2), 95.1 (*d*, C-8), 101.8 (*s*, C-4a), 102.3 (*d*, C-3′), 106.9 (*s*, C-6), 115.5 (*s*, C-5′), 118.1 (*s*, C-1′), 122.8 (*d*, –CH=C<), 123.5 (*d*, –CH=C<), 127.3 (*d*, C-6′), 130.1 (*s*, –CH=C<), 130.6 (*s*, –CH=C<), 153.2 (*s*, C-2′), 155.5 (*s*, C-4′), 160.2 (*s*, C-8a), 161.2 (*s*, C-5), 164.3 (*s*, C-7), 197.1 (*s*, C-4). MS: Scheme 1.

Acetylation of **1** (**1a**). A soln of **1** (10 mg) in a mixture of Ac_2O (0.5 ml) and C_5H_5N (0.5 ml) was allowed to stand at room temp. overnight, and the reaction mixture was worked-up in the usual manner. **1a** (4.5 mg) was obtained as an oily product. $FeCl_3$ (−), Gibbs test (−). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1270, 1190 (ester), 1690 (C=O), 1610, 1500 (arom. C=C). ^{1}H NMR ($CDCl_3$): δ 1.57, 1.64, 1.69, 1.74 (each 3 H, each *s*, Me × 4), 2.37 (3 H, *s*, –OAc), 2.31 (6 H, *s*, –OAc × 2), 2.27 (3 H, *s*, –OAc), 2.6–3.0 (2 H, *m*, H_2-3), 3.24 (4 H, *br d*, *J* = 7.5 Hz, Ar–CH$_2$–CH= × 2), 5.05, 5.21 (each 1 H, each *br t*, *J* = 7.5 Hz, –CH$_2$–CH=C< × 2), 5.55 (1 H, *dd*, *J* = 11.8 and 3.7 Hz, H-2), 6.53 (1 H, *s*, H-8), 6.94 (1 H, *s*, H-3′), 7.48 (1 H, *s*, H-6′). MS *m/z*: 592 $[M]^+$, 550 $[M - CH_2CO]^+$, 508 $[M - CH_2CO \times 2]^+$, 466 $[M - CH_2CO \times 3]^+$, 424 $[M - CH_2CO \times 4]^+$, 43 (MeCO) base peak.

Acid-catalysed cyclization of **1** (*formation of* **1b**). A soln of **1** (10 mg), conc. HCl (1.0 ml) and MeOH (5.0 ml) was refluxed for 2 hr. The reaction mixture was diluted with H_2O and extracted with Et_2O. The Et_2O extract was evaporated to dryness *in vacuo*, and the residue was purified by chromatography on Si gel with C_6H_6 to give a colorless oil (**1b**) (1.5 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1650 (C=O), 1590, 1510 (arom. C=C). ^{1}H NMR ($CDCl_3$): δ 1.33 (12 H, *s*, ) (CH_3)$_2$ × 2), 1.79 (4 H, *br t*, *J* = 7.1 Hz, Ar–CH$_2$–CH$_2$– × 2), 2.63 (2 H, *t*, *J* = 7.1 Hz, Ar–CH$_2$–CH$_2$), 2.71 (2 H, *t*, *J* = 7.1 Hz, Ar–CH$_2$–CH$_2$–), 2.8–3.4 (2 H, *m*, H_2-3), 5.9 (1 H, *br s*, OH; disappeared on the addition of D_2O), 5.96 (1 H, *s*, H-8), 6.33 (1 H, *s*, H-3′), 6.93 (1 H, *s*, H-6′), 12.4 (1 H, *s*, OH-5; disappeared on the addition of D_2O). MS *m/z*: 424 $[M]^+$, 406 $[M - H_2O]^+$ base peak, 363 $[406 - C_3H_7]^+$, 351 $[406 - C_4H_7]^+$, 220 (retro-Diels–Alder cleavage; A-ring), 204 (retro-Diels–Alder cleavage; B-ring), 165 $[220 - C_4H_7]^+$, 149 $[204 - C_4H_7]^+$.

Euchrestaflavanone C (**2**). Pale yellow needles (from C_6H_6–n-C_6H_{14}), mp 198–200°, $[\alpha]_D^{22}$ − 103.1° (EtOH; *c* 0.8). Found: M^+ 422.1729; $C_{25}H_{26}O_6$ requires 422.1732. HPLC R_t: 6.0 min. UV λ_{max}^{EtOH} nm (log ϵ): 293 (3.93), 342 sh (3.23); + NaOAc: 294 (3.55), 340 (3.28); + $AlCl_3$: 312 (3.59); + NaOEt: 332 (3.87). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1640 (C=O), 1610, 1600, 1510 (arom. C=C). ^{13}C NMR (DMSO-d_6): δ 17.5 (*q*, Me), 21.3 (*t*, –CH$_2$–CH=C<), 25.6 (*q*, Me), 27.8 (*q*, Me × 2), 41.2 (*t*, C-3), 73.6 (*d*, C-2), 76.2 (*s*, ), 95.3 (*d*, C-8), 101.7 (*s*, C-4a), 102.9 (*d*, C-3′), 106.9 (*s*, C-6), 112.8 (*s*, C-5′), 117.6 (*s*, C-1′), 121.6 (*d*, ), 122.7 (*d*, –CH=C<), 124.9 (*d*, ), 127.7 (*d*, C-6′), 130.1 (*s*, –CH=C<), 153.5 (*s*, C-2′), 155.5 (*s*, C-4′), 160.1 (*s*, C-8a), 161.2 (*s*, C-5), 164.3 (*s*, C-7), 196.9 (*s*, C-4). MS *m/z*: 422 $[M]^+$, 407 $[M - Me]^+$, 404 $[M - H_2O]^+$, 389 $[M - (Me + H_2O)]^+$, 220, 202, 187, 165. CD: $\Delta\epsilon_{337} + 0.64$, $\Delta\epsilon_{289} - 0.97$, $\Delta\epsilon_{256} + 0.03$.

Acetylation of **2** (**2a**). The same procedures described for acetylation of **1** were carried out to give a colorless oil (**2a**) (4.9 mg), negative $FeCl_3$ and Gibbs tests. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1260, 1180 (ester), 1680 (C=O), 1630, 1580 (arom. C=C). ^{1}H NMR ($CDCl_3$): δ 1.26, 1.44 (each 3 H, each *s*, Me × 2), 1.56 (6 H, *s*, Me × 2), 2.26 (3 H, *s*, –OAc), 2.30 (3 H, *s*, –OAc), 2.37 (3 H, *s*, –OAc), 2.6–3.1 (2 H, *m*, H_2-3), 3.20 (2 H, *br d*, *J* = 7.3 Hz, Ar–CH$_2$–CH=), 5.06 (1 H, *br t*, *J* = 7.3 Hz, –CH$_2$–CH=C<), 5.47 (1 H, *dd*, *J* = 12.5 and 3.4 Hz, H-2), 5.63 (1 H, *d*, *J* = 10.0 Hz, ), 6.31 (1 H, *d*, *J* = 10.0 Hz, ), 6.51 (1 H, *s*, H-8), 6.55 (1 H, *s*, H-3′), 7.16 (1 H, *s*, H-6′). MS *m/z*: 548 $[M]^+$, 506 $[M - CH_2CO]^+$, 464 $[M - CH_2CO \times 2]^+$, 422 $[M - CH_2CO \times 3]^+$, 43 (MeCO) base peak.

5,7,4′-*Trihydroxy*-6,8-*diprenylisoflavone* (**3**). Colorless needles (from n-C_6H_{14}–Me_2CO), mp 140–142°. Found: M^+ 406.1781; $C_{25}H_{26}O_5$ requires 406.1786. HPLC R_t: 7.2 min. ^{13}C NMR (DMSO-d_6): δ 17.8 (*q*, Me × 2), 21.5 (*t*, –CH$_2$–CH=C< × 2), 25.5 (*q*, Me × 2), 105.0 (*s*, C-4a), 106.4 (*s*, C-8), 111.8 (*s*, C-6), 115.3 (*d*, C-3′, C-5′), 121.7 (*s*, C-1′), 122.2 (*s*, C-3), 122.7 (*d*, –CH=C< × 2), 130.5 (*d*, C-2′, C-6′), 131.1 (*s*, –CH=C<), 131.4 (*s*, –CH=C<), 153.3 (*s*, C-8a), 154.2 (*s*, C-2), 157.2 (*s*, C-4′), 157.8 (*s*, C-5), 159.4 (*s*, C-7), 181.1 (*s*,

C-4). This was identified by direct comparison (mmp, HPLC, TLC and IR) with an authentic sample [4].

Warangalone (scandenone) (**4**) [5, 6]. Pale yellow needles (from n-C_6H_{14}), mp 165–166°. Found: M^+ 404.1622; $C_{25}H_{24}O_5$ requires 404.1609. HPLC R_t: 17.2 min.

Osajin [7]. Pale yellow needles (from n-C_6H_{12}), mp 194–195°. Found: M^+ 404.1622; $C_{25}H_{24}O_5$ requires 404.1620. HPLC R_t: 15.8 min.

Naringenin. ^{13}C NMR (DMSO-d_6): 95.0 (C-8), 95.8 (C-6).

Euchrestaflavanone A. ^{13}C NMR (DMSO-d_6): 95.2 (C-8), 106.8 (C-6).

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