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THREE PRENYLFLAVANONES FROM *EUCHRESTA JAPONICA*

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Key Word Index—*Euchresta japonica*; Leguminosae; euchrenone a_1; euchrenone a_2; euchrenone a_3; prenylflavanone.

Abstract—Three new prenylflavanones, euchrenone a_1– a_3, were isolated from the roots of *Euchresta japonica*. Their structures were established by spectroscopic methods and by synthesis.

INTRODUCTION

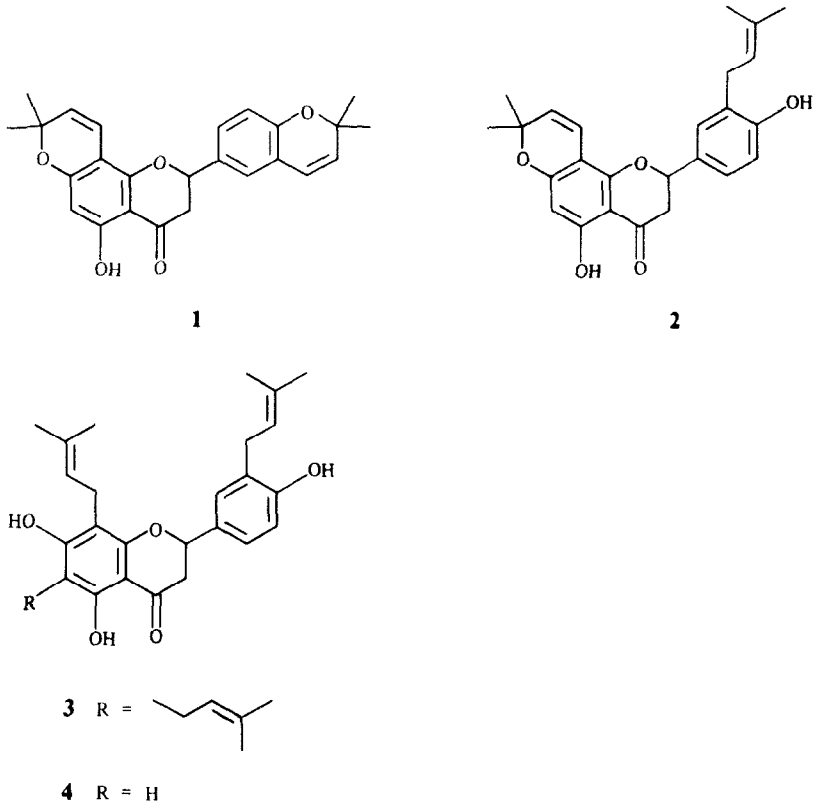
The legume genus *Euchresta* is peculiar to East Asia, where five species have been recognized. These plants show significant morphological and ecological differences [1–3]. In Japan, the roots of *E. japonica* Hook. f. ex Regel have been used traditionally as a substitute for *Sophora tonkinensis* Gagnep. for the treatment of tumours [4]. Up to the present, lupin alkaloids [5, 6], prenylflavanones and isoflavones [7–9] have been isolated from the roots. In this paper, we describe the isolation and characterization of three new flavanones, designated euchrenone a_1–a_3 from the roots of *E. japonica*.

RESULTS AND DISCUSSION

Euchrenone a_1 (**1**), $C_{25}H_{24}O_5$ ([M^+] 404.1623, calcd 404.1623), gave positive tests both with ferric chloride (greenish-brown) and Mg–HCl (purple). Its UV spectrum (271, 296 and 308sh nm) suggested the presence of a flavanone skeleton. In the ^{1}H NMR spectrum, two double doublets (J = 3.1 and 17.1 Hz, and 12.9 and 17.1 Hz) at δ2.77 and 3.06 and a double doublet (J = 3.1 and 12.9 Hz) at δ5.31 ppm were assignable to H_2-3 and H-2, respectively. The ^{1}H NMR spectrum also showed the presence of two 2,2-dimethylpyran units as four methyls at δ1.42, 1.44, 1.45 and 1.55 and four methylene protons at δ5.46, 5.66, 6.33 and 6.53, and a chelated hydroxy group (δ12.0). A typical ABX system at δ6.81 (*d*, J = 8.4 Hz), 7.05 (*d*, J = 2.2 Hz) and 7.18 (*dd*, J = 2.2, 8.4 Hz) established the presence of three aromatic protons in the B moiety, while a singlet at δ5.99 showed the presence of a single aromatic proton in the A moiety. In the MS, the molecular ion was detected at *m/z* 404. Other prominent fragments are shown in Fig. 1. Fragment ion peaks at *m/z* 218 and 186 were caused by the usual RDA fragmentation. The subsequent loss of a methyl group from each of these ions established that both the A-ring and the B-ring contained a fused 2,2-dimethyl pyran unit. From the spectral data described above, euchrenone a_1 was deduced to be 5-hydroxy-[6″,6″-dimethylpyrano (2″,3″:7,8)]-[6‴,6‴-dimethylpyrano (2‴,3‴:4′,3′)] flavanone or the alternative structure of 5-hydroxy-[6″,6″-dimethylpyrano (2″,3″:7,6)]-[6‴,6‴-dimethylpyrano (2‴,3‴:4′,3′)] flavanone. To distinguish between these two possibilities, euchrestaflavanone A (**4**) (revised structure) [9] was oxidized by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [10]. The resultant compound was

Table 1. ^{1}H NMR data for compounds **1**–**3** (270 MHz, $CDCl_3$, TMS as int. standard)

H	1	2	3
2	5.31 (1H, *dd*, J = 12.9, 3.1 Hz)	5.31 (1H, *dd*, J = 12.9, 3.1 Hz)	5.25 (1H, *dd*, J = 12.9, 3.1 Hz)
3	2.77 (1H, *dd*, J = 17.1, 3.1 Hz)	2.77 (1H, *dd*, J = 17.1, 3.1 Hz)	2.78 (1H, *dd*, J = 17.1, 3.1 Hz)
	3.06 (1H, *dd*, J = 17.1, 12.9 Hz)	3.06 (1H, *dd*, J = 17.1, 12.9 Hz)	3.01 (1H, *dd*, J = 17.1, 12.9 Hz)
6	5.99 (1H, *s*)	5.97 (1H, *s*)	
2′	7.05 (1H, *d*, J = 2.2 Hz)	7.07 (1H, *d*, J = 2.2 Hz)	7.10 (1H, *d*, J = 2.2 Hz)
5′	6.81 (1H, *d*, J = 8.4 Hz)	6.83 (1H, *d*, J = 8.4 Hz)	6.83 (1H, *d*, J = 8.4 Hz)
6′	7.18 (1H, *dd*, J = 8.4, 2.2 Hz)	7.12 (1H, *d*, J = 8.4, 2.2 Hz)	7.21 (1H, *dd*, J = 8.4, 2.2 Hz)
Chromene ring	5.46, 5.66 (1H, each *d*, J = 10 Hz)	5.44 (1H, *d*, J = 10 Hz)	
	6.33, 6.53 (1H, each *d*, J = 10 Hz)	6.52 (1H, *d*, J = 10 Hz)	
Isoprenyl		1.42, 1.44 (3H, each *s*, Me)	1.40 (3H, *s*, Me)
		3.38 (2H, *d*, J = 6.2 Hz, $-CH_2-$)	1.48 (6H, *s*, 2 × Me)
		5.34 (1H, *t*, J = 6.2 Hz, $-CH=C<$)	1.50 (3H, *s*, Me)
			3.30–3.40 (6H, *m*, 3 × $-CH_2-$)
			5.20–5.34 (3H, *m*, 3 × $-CH=C<$)



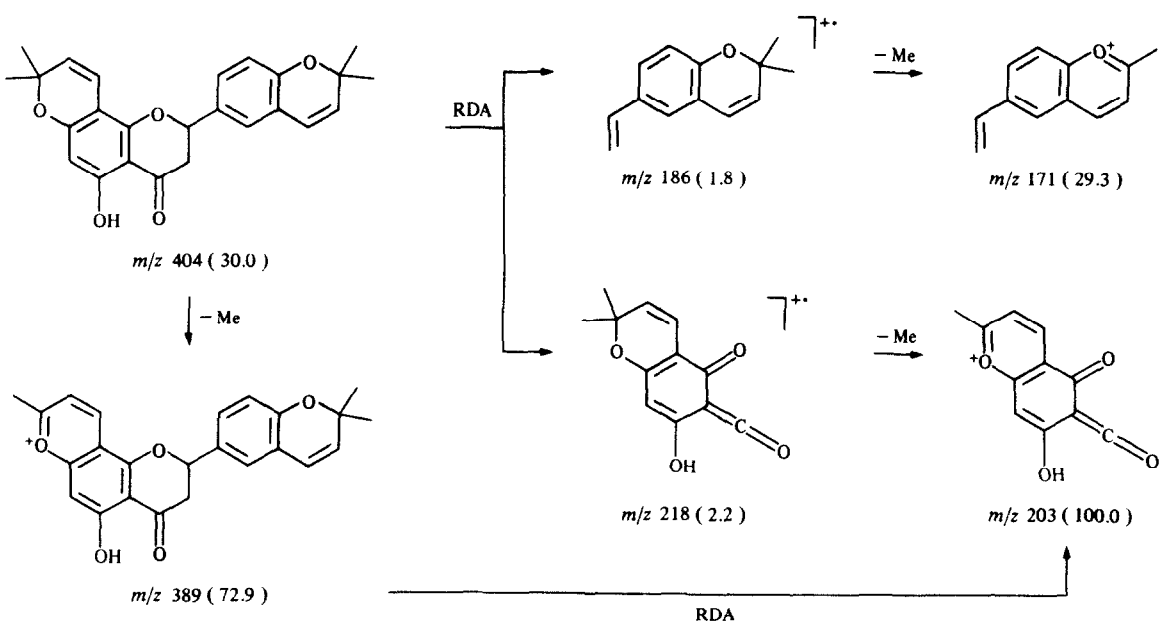
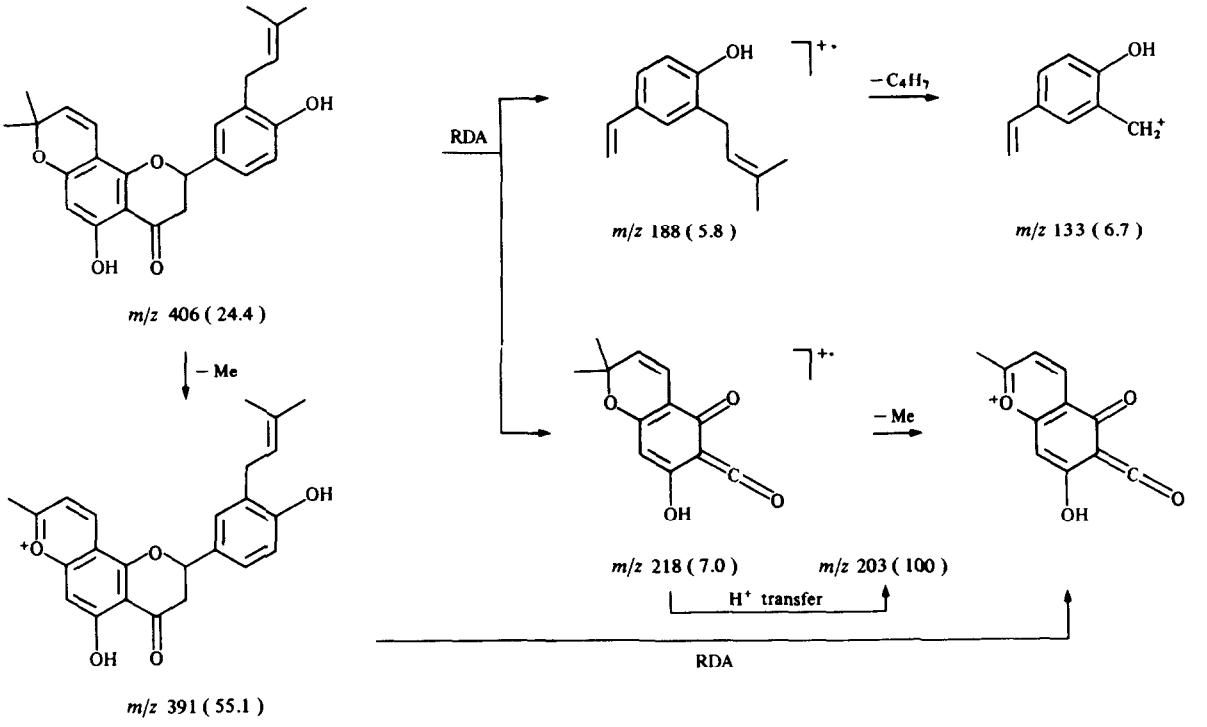


Fig. 1.

completely identical with **1** (mp, Co-TLC and ^{1}H NMR). Consequently, the structure of euchrenone a_1 was confirmed as **1**.

Euchrenone a_2(**2**), $C_{25}H_{26}O_5$ ([M^+] 406.1781, calcd 406.1780). In general, the spectral data and colour tests of this compound were similar to those of euchrenone a_1. The most conspicuous differences between the two were as follows: euchrenone a_2 differed from a_1 by two mass unit and possessed another hydroxy group (δ5.25) in addition to a chelated hydroxy group (δ12.32). In the ^{1}H NMR spectrum, in addition to a 2,2-dimethylpyran unit, a typical set of signals based on an isoprenyl group



was observed at δ1.42, (*s*, Me), 1.44 (*s*, Me), 3.38 (*d*, J = 6.2 Hz, CH_2), and 5.34 (*t*, J = 6.2 Hz, –CH=). Other signals established the substitution pattern of euchrenone a_2 (A ring: δ5.99 *s*; B ring: an ABX system) was the same as that of euchrenone a_1. These data led to the conclusion that in a_2, one of the chromene rings of a_1 was opened to form an isoprenyl residue. The fragment peaks at *m/z* 218 and 203 were attributable to the A ring. On the other hand, ion peaks at *m/z* 188 and 133 [188–C_4H_7] were attributed to fragments based on the B ring and suggested the structure of euchrenone a_2 was 5,4′-dihydroxy-3′-(γ,γ-dimethylallyl)-[6″,6″-dimethylpyrano (2″,3″:7,8)]flavanone. The synthetic product prepared from **4** in the way described above furnished a confirmation of the structure as **2**.

Euchrenone a_3 (**3**), $C_{30}H_{36}O_5$ ([M^+] 476.2563, calcd 476.2562). Its UV spectrum (232sh, 297 and 350 nm) suggested the compound was also a flavanone derivative. The ^{1}H NMR spectrum showed the presence of three isoprenyl groups and three hydroxy groups. Three aromatic protons based on the B ring were observed, but aromatic protons of the A ring were not. In the MS, a significant ion peak was observed at *m/z* 288 in addition to the molecular ion peak (*m/z* 476). The ion peak based on the A-ring yielded two fragments of *m/z* 233 [$M-C_4H_7$]$^+$ and 177 [$M-2\times C_4H_7$]$^+$. These data showed the A ring possessed two isoprenyl groups at C-6 and C-8, and the B ring had one isoprenyl group at C-3′. Therefore, the structure of euchrenone a_3 was established as 5,7,4′-trihydroxy-6,8,3′-tri-(γ,γ-dimethylallyl) flavanone (**3**). The constituents contained in the polar fractions are now being investigated.

EXPERIMENTAL

Mps: uncorr. ^{1}H NMR spectra were obtained at 270 MHz using TMS as int. standard. MS were recorded at 70 eV with a direct inlet system.

Plant material. Whole plants of *Euchresta japonica* were collected at Mt Taradake, Nagasaki Prefecture (Kyushu), Japan in Oct 1985. A voucher is deposited at the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation of compounds **1–3**. Dried cut roots (1.0 kg) of *E. japonica* were crushed into pieces and extracted with MeOH under reflux (12 hr × 8). The MeOH soln was concentrated *in vacuo* and the combined extract (380 g) was subjected to silica gel CC using C_6H_6 as a solvent to give crude compounds **1–3**, which were rechromatographed on silica gel eluted with C_6H_{14}–EtOAc (10:1). The fractions which contained **1**, **2** and **3** were purified by recrystallization or PLC to give euchrenone a_1 (**1**) (28 mg), a_2 (**2**) (20 mg) and a_3 (**3**) (45 mg).

Euchrenone a_1 (**1**). Pale orange rectangles (from C_6H_{14}–Et_2O), mp 120–122°, R_f 0.50 (C_6H_{14}–EtOAc, 4:1), Found: M^+ 404.1623 (calcd 404.1623). UV λ_{max}^{MeOH} nm (log ε): 224 (4.61), 263sh (4.53), 271 (4.59), 296 (4.05), 308sh (3.96), 360 (3.48); λ^{+NaOMe}: 278, 310sh, 384; $\lambda + AlCl_3$: 272, 281, 323, 365; $\lambda^{+AlCl_3/HCl}$: 272, 281, 322, 365; λ + NaOAc: 263sh, 271, 296, 308sh, 360; λ^{+NaOAc/H_3BO_3}: 263sh, 270, 296, 307sh, 360. MS *m/z* (rel. int.): 404 (30.0), 389 (72.9), 219 (5.6), 218 (2.2), 204 (14.7), 203 (100), 187 (22.2), 171 (29.3), 149 (5.6).

Euchrenone a_2 (**2**). Pale yellow plates (from C_6H_{14}), mp 145–146°. R_f 0.52 (C_6H_{14}–EtOAc, 9:4). Found: M^+ 406.1781 (calcd 406.1780). UV λ_{max}^{MeOH} nm (log ε): 228sh (4.29), 271 (4.60), 295 (3.96), 305sh, (3.85), 360 (3.61); λ^{+NaOMe}: 247, 279, 305sh, 420; λ^{+AlCl_3}: 232, 240, 272sh, 281, 324, 363; $\lambda^{+AlCl_3/HCl}$: 232, 241sh,

272sh, 281, 323, 365; λ^{+NaOAc}: 271, 296sh, 308sh, 360; λ^{+NaOAc/H_3BO_3}: 271, 295sh, 308sh, 358. MS *m/z* (rel. int.): 406 (24.4), 391 (55.1), 219 (7,0), 218 (4.4), 203 (100), 188 (5.8), 133 (6.7).

Euchrenone a_3 (**3**). A pale yellow powder (from C_6H_{14}), mp 70–72°. R_f 0.34 (C_6H_{14}–EtOAc, 9:4). Found: M^+ 476.2563 (calcd 476. 2562) UV λ_{max}^{MeOH} nm (log ε): 232sh (4.39), 297 (4.15), 350 (3.32); λ^{+NaOMe}: 246sh, 296sh, 342; λ^{+AlCl_3}: 231, 308, 362; $\lambda^{+AlCl_3/HCl}$: 229, 276sh, 313, 362; λ^{+NaOAc}: 300, 342; λ^{+NaOAc/H_3BO_3}: 297, 347. MS *m/z* (rel. int.): 476 (100), 461 (13.2), 433 (10.0), 421 (34.2), 405 (22.4), 377 (10.7), 365 (17.3), 288 (14.9), 273 (32.0), 260 (25.1), 245 (22.0), 233 (55.3), 232 (29.9), 217 (31.5), 204 (13.9), 189 (65.3), 188 (8.0), 177 (43.2), 133 (21.1).

Synthesis of euchrenones a_1 *and* a_2 *from euchrestaflavanone A.* A dry C_6H_6 soln containing euchrestaflavanone A (**4**) (70 mg, 0.17 mmol) and DDQ (100 mg, 0.44 mmol) was stirred for 5 hr at room temp. After filtration, the filtrate was subjected to CC on silica gel (C_6H_{14}–EtOAc, 10:1) to give **1** (12 mg) and **2** (7 mg). Compd. **1**: mp 127–129°; MS *m/z* (rel. int.): 404 [M^+] (30.0), 389 (81.1), 219 (3.3), 218 (4.8), 204 (11.8), 203 (100), 187 (22.2), 171 (27, 7). Compd. **2**: mp 144–145°; MS *m/z* (rel. int.) 406 [M^+] (24.0), 391 (56.2), 219 (7.1), 218 (4.4), 204 (12.4), 203 (100), 188 (5.8), 133 (6.0). Compds **1** and **2** were identical to euchrenone a_1 and a_2 (direct comparisons).

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