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COUMARONOCHROMONES FROM THE STEMS OF *EUSCHRESTA FORMOSANA*

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Key Word Index—*Euchresta formosana*; Leguminosae; coumaronochromone; euchretin B; euchretin C.

Abstract—Two new coumaronochromones, named euchretins B and C, were isolated from the stems of *Euchresta formosana* in addition to a known coumaronochromone, euchretin A. By means of the spectroscopic data, the structures of euchretines B and C were determined to be 8,3′-di (γ,γ-dimethylallyl)-5,7,4′,5′-tetrahydroxy- and 6,8,3′-tri (γ,γ-dimethylallyl)-5,7,4′,5′-tetrahydroxycoumaronochromone respectively.

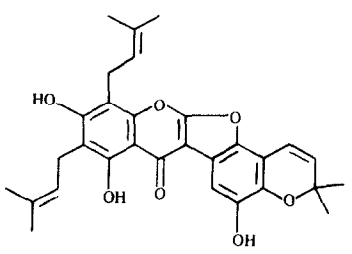
INTRODUCTION

In continuation of our chemotaxonomic studies on the genus *Euchresta*, we have reported several new prenylated flavonoids from *E. japonica* [1–4]. As a result of our interest in the flavonoid compounds in *E. japonica*, our attention was drawn to the chemical constituents of *E. formosana* (Hayata) Ohwi because the species has been hypothesized to evolve from proto-*Euchresta* by a different pathway from *E. japonica* [5]. It has been used in folk medicines as a pain-killer, particularly for the throat and for snake wounds in Taiwan [6]. Our present investigation on the constituents of the stems of this plant resulted in the isolation of two novel coumaronochromones. The structure elucidation of which is described in this paper.

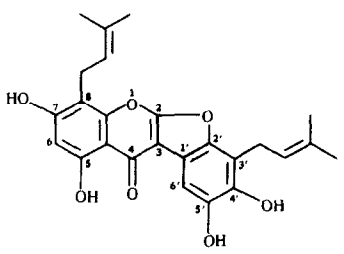
RESULTS AND DISCUSSION

Compound **1**, mp 208–209°, $C_{30}H_{36}O_7$ (M^+: *m/z* 502.1992, calcd. 502.1991), was identified as euchretin A. This was previously isolated from the stems of *E. japonica* [3].

Compound **2**, mp 242–243°, $C_{25}H_{24}O_7$ (M^+: *m/z* 436.1501, calcd. 436.1521), was also obtained as a colourless powder. The ^{1}H NMR spectrum contained, two two-proton doublets ($J = 7.3$ Hz) at δ3.52 and 3.62, two one-proton triplets ($J = 7.3$ Hz) at δ5.26 and 5.38 and four methyl groups at δ1.68, 1.70, 1.86 and 1.89. This suggested that **2** had two γ,γ-dimethyllalyl groups. Furthermore, four one-proton singlets at δ7.53, 8.77, 9.69 and 12.59 showed the presence of four hydroxyl groups. Each absorption band in the IR (3450 and 1650 cm^{-1}; chelated OH and >C=O) and the UV (260, 288, 308sh and 348 nm) spectra indicated **2** was an isoflavone derivative. A coumaronochromone structure was indicated by the absence of a characteristic signal due to a proton at C-2 (*ca* 8 ppm) in the ^{1}H NMR spectrum. Two aromatic protons appeared at δ6.40 and 7.34. The latter signal was assigned to a proton at C-6′ which was shielded diamagnetically by an adjacent carbonyl group. The former was assigned to a proton on the A ring. By comparison with the known structure of euchretin A (**1**), the four hydroxyl groups were assigned at C-5, 7, 4′ and 5′, and one of two γ,γ-dimethylallyl groups was placed at C-3′. Hence the other γ,γ-dimethylallyl group had to be at either C-6 or C-8. In the ^{13}C NMR of the permethyl ether of **2**, four methoxyl carbons were observed at δ55.99, 56.20, 56.66 and 61.31. The last signal in the low-field was assigned to C-4′. This finding suggested that all the methoxy groups, except C-4′, were not sandwiched betweeen any substituents. Hence the position of the γ,γ-dimethylallyl group on the A ring was deduced to be at C-8. Consequently, the structure of **2** was concluded to be 8,3′-di(γ,γ-dimethylallyl)-5,7,4′,5′-tetrahydroxy coumaronochromone, which we have named euchretin B.



1



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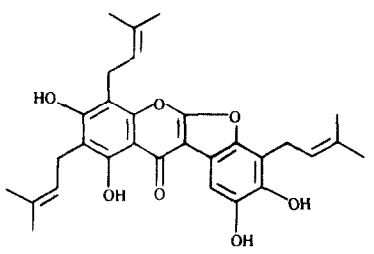

3

Compound **3**, mp 215° (dec.), $C_{30}H_{32}O_7$ (M^+: *m/z* 504.2146, calcd. 504.2148), was obtained as colourless needles. All the spectral data were similar to those of **1** and **2**. These results suggested that **3** had a coumaronochromone skeleton. In the ^1H NMR, four hydroxyl groups at δ7.56, 8.34, 8.81 and 13.33, three γ,γ-dimethylallyl groups [δ1.67, 1.69, 1.70, 1.79, 1.86 and 1.89 (3H, *s*, Me), 3.45 (2H, *d*, J=6.9 Hz CH_2), 3.59 (4H, *m*, 2 × CH_2), 5.22–5.39 (3H, *m*, 3 × CH=C<)] and only a single aromatic proton (δ7.35) assignable to H-6′, were observed. The UV spectra data suggested that **3** had the same oxygenation pattern as **1** and **2**. Therefore, it could be concluded that **3** had the same partial structure as **1** about the A ring moiety and had the same one as **2** about the B ring. Consequently, the structure of **3** was confirmed to be 6,8,3′-tri(γ,γ-dimethylallyl)-5,7,4′,5′-tetrahydroxycoumaronochromone, which we have named euchretin C. A facile distinction of **2** and **3** from other compounds is provided by the observation that each UV band I undergoes an abnormal bathochromic shift to 580–590 nm upon addition of sodium methoxide, due to the formation of *ortho* quinone.

Other flavonoid compounds in the stems as well as the roots of *E. formosana* are now being investigated.

EXPERIMENTAL

Plant material. The stems of *Euchresta formosana* were collected in Taipei (Taiwan) in Aug. 1987. Voucher specimens are deposited at the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation of compounds **1–3**. Dried stems (250 g) of *E. formosana* were crushed into pieces and extracted with CH_2Cl_2, Me_2CO and MeOH, successively. The CH_2Cl_2 soln was concentrated *in vacuo* to give a greenish-gum (12 g), which was subjected to silica gel CC. Fractions eluted *n*-hexane–Me_2CO (5:1) contained a mixture of **1–3**. The mixture was further purified by CC (*n*-hexane–Me_2CO) and the separated compounds were recrystallized to give **1** (5 mg), **2** (25 mg) and **3** (32 mg).

Euchretin B (**2**). $C_{25}H_{24}O_7$, M_r 436.1501 (calcd 436.1521), a colourless powder ($CHCl_3$–Et_2O), mp 208–209°. EIMS (*m/z*) (rel. int.): 436 (95) $[M]^+$, 421 (7) $[M-Me]^+$, 419 (13), 393 (5) $[M-C_3H_7]^+$, 380 (100), 365 (60), 337 (7), 325 (30), 312 (37), 203 (17), 189 (13), 165 (13); IR (ν^{KBr} cm^{-1}): 3450, 1650, 1610, 1595; UV λ^{MeOH} nm (log ε): 260 (4.5), 288 (4.2), 308sh (4.0), 348 (4.0); +NaOMe 270, 315, 356, 580 (dec.); +$AlCl_3$ 273, 304, 370, 398; +$AlCl_3$/HCl 269, 280sh, 294sh, 390; +NaOAc 253, 294sh, 308sh, 324sh; +NaOAc/H_3BO_3 263, 292, 305, 356; ^1H NMR (Me_2CO-d_6, 270 MHz): δ1.68, 1.70, 1.86, 1.89 (3H, each *br*, Me), 3.52, 3.62 (2H, each *br d*, J=7.3 Hz, CH_2CH=C<), 5.26, 5.38 (1H, each *br t*, J=7.3 Hz, CH=C<), 6.40 (1H, *s*, H-6), 7.34 (1H, *s*, H-6′), 7.53, 8.77, 9.69 (1H, each *s*, OH), 12.95 (1H, *s*, C_5-OH).

Euchretin B permethylether: **2** (15 mg) was methylated with MeI–K_2CO_3 in Me_2CO to give the permethyl ether (12 mg), colourless needles (MeOH), mp 197–198° (MeOH). EIMS (*m/z*) (rel. int): 492 $[M]^+$ (100: $C_{29}H_{32}O_7$); ^1H NMR ($CDCl_3$, 270 MHz): δ1.70 (6H, *br s*, 2 × Me), 1.86, 1.87 (3H, each *br s*, Me), 3.55, 3.61 (2H, each *br d*, J=7.3 Hz, CH_2C=C<), 3.86, 3.94, 3.97, 4.02 (3H, each *s*, OMe), 5.20, 5.32 (1H, each *br t*, J=7.3 Hz, CH=C<), 6.49 (1H, *s*, H-6), 7.56 (1H, *s*, H-6′); ^{13}C NMR ($CDCl_3$): δ17.83, 17.87, 25.78, 15.85 (Me), 22.06, 23.48 (CH_2), 121.58, 121.63 (CH=C<), 132.35, 132.60 (CH=C<), 174.5 (>C=O), 55.99, 56.20, 56.55, 61.31 (OMe).

Euchretin C (**3**). $C_{30}H_{32}O_7$, M_r 504.2146 (Calcd 504.2148), colourless needles (C_6H_6–*n*-hexane), mp 215° (dec.). EIMS (*m/z*) (rel. int.): 504 (92) $[M]^+$, 461 (74), 449 (58), 433 (21), 407 (39), 393 (100), 377 (13), 349 (19), 337 (22), 189 (16); IR ν^{KBr} cm^{-1}: 3450, 1645, 1610. UV λ^{MeOH} nm: 263, 288, 350; +NaOMe 262, 278, 310, 370, 590 (dec.); +$AlCl_3$ 265, 295, 318sh, 349; +$AlCl_3$/HCl 264, 288, 308sh, 349; +NaOAc 264, 290, 305sh, 354; +NaOAc/H_3BO_3 267, 293, 313sh, 365. ^1H NMR (Me_2CO-d_6): δ1.67, 1.69, 1.70, 1.79, 1.86, 1.89 (3H, each *br s*, Me), 3.45 (2H, *br d*, J=6.9 Hz, CH_2), 3.59 (4H, *m*, 2 × CH_2), 5.22–5.39 (3H, *m*, 3 × CH=C<), 7.35 (1H, *s*, H-6′), 7.56, 8.34, 8.81 (1H, *s*, OH), 13.33 (1H, *s*, C_5-OH).

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