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SIX FLAVANONES FROM THE ROOTS OF *EUCHRESTA FORMOSANA*

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Key Word Index—*Euchresta formosana*; Leguminosae; prenylflavanone; xambioona; euchrenone a_5; euchrenone a_6.

Abstract—Two new flavanones, euchrenones a_5 and a_6, were isolated from the roots of *Euchresta formosana* in addition to four known flavanones (xambioona, euchrestaflavanones A, B and C) and a pterocarpan (maackiain). By spectroscopic analysis, the structures of euchrenones a_5 and a_6 were determined to be 7-hydroxy-8-γ,γ-dimethylallyl[6‴,6‴-dimethylpyrano(2‴,2‴: 4′,3′)]- and 5,7,2′-trihydroxy-6,8-di(γ,γ-dimethylallyl)-[6⁗,6⁗-dimethylpyrano (2⁗,3⁗: 4′,3′)]flavanone, respectively.

INTRODUCTION

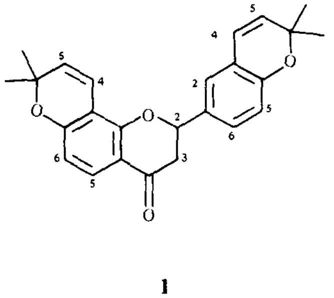
In continuing chemotaxonomic studies on the genus *Euchresta* (Leguminosae), we have reported several flavanones [1, 2], isoflavones [2, 3] and coumaronochromones [4, 5]. The present investigation was directed to the constituents of roots of *E. formosana* (Hayata) Ohwi, and resulted in the isolation and identification of two new flavanones, euchrenones a_5 and a_6.

RESULTS AND DISCUSSION

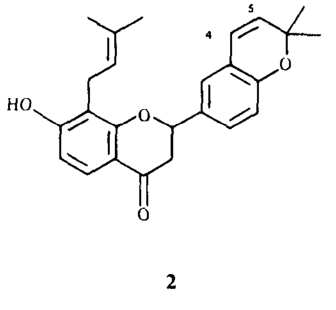
The dried roots of *E formosana* were extracted to give three compounds (**1**–**3**) in pure form. Furthermore, the known compounds, euchrestaflavanones A, B and C and maackiain [6, 7], were also obtained from more polar fractions

Compound **1**, $C_{25}H_{24}O_4$, was obtained as a light yellow amorphous powder. In the ^{1}H NMR spectrum, three typical double doublets at 5.35 (1H, $J = 13\,2$ and 2.9 Hz), 2 78 (1H, $J = 16.9$ and 2.9 Hz) and 3.00 (1H, $J = 16.9$ and 13 2 Hz) assignable to H-2 and H-3 of a flavanone skeleton were observed. The spectral data exhibited the signals of four singlets at δ1.44, 1.45, 1.46 and 1.47 (Me) and four doublets ($J = 9.9$ Hz) at δ5.55, 5.64, 6.33 and 6.63 based on the *cis*-olefinic protons. In the MS, the prominent fragment peaks at m/z 187 and 171 showed that chromene rings were located at both A and B rings. Furthermore, the ^{1}H NMR spectral data showed that signals of B ring at δ6.89 (1H, *d*, $J = 8.4$ Hz), 7.06 (1H, *d*, $J = 2.2$ Hz) and 7 19 (1H, *dd*, $J = 8.4$, 2.2 Hz), which was very similar to those of euchrenone a_1 [1] Two *ortho*-coupled aromatic protons at 6.48 and 7.73 ppm could be assigned to H-6 and H-5 in A ring. Consequently, **1** is [6″,6″-dimethylpyrano (2″,3″: 7,8)]-[6‴,6‴-dimethylpyrano (2‴,3‴: 4′,3′)] flavanone This compound was previously isolated from the seeds of *Calopogonium mucunoides* [8] and named xambioona.

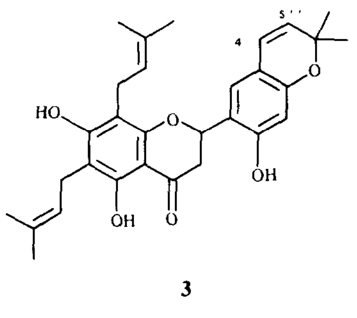
Compound **2**, $C_{25}H_{26}O_4$, was obtained as a light yellow amorphous powder. In the ^{1}H NMR spectrum, three typical double doublets at δ5 35 (1H, $J = 13.2$ and 2.9 Hz), 2.77 (1H, $J = 16.7$ and 2.9 Hz) and 3.01 (1H, $J = 16.7$ and 13.2 Hz) assignable to H-2 and H-3 of a flavanone skeleton were observed. The spectral data further indicated the presence of a γ,γ-dimethylallyl group [1.75 (6H, *s*, 2 × Me), 3 42 (2H, *d*, $J = 7$ Hz, CH_2), 5.29 (1H, *br t*, $J = 7$ Hz, CH=C<)] and a chromene ring [1.48 (6H, *s*, 2 × Me), 5.65, 6.32 (1H, each *d*, $J = 9.9$ Hz)] The positional problem whether a chromene ring was located at A or B ring was resolved as follows: two olefinic protons assigned to H-4″ or/and H-4‴ of euchrenone a_1 (**8**) appeared at δ6.33 and 6.53, whereas a corresponding proton of euchrenone a_2 [1] appeared at δ6 52 assigned to H-4″. This evidence that a signal at δ6.32 of **2** could be assigned to H-4‴ by its similarity of the chemical shift proved that the chromene ring was fused with B ring. The deduction was also supported by the MS, that is, a significant fragment caused by demethylation of B_1^+ at



1



2



3

m/z 171 was exactly the same as observed in **8**. Furthermore, the chemical shifts corresponding to the protons of A and B rings were superimposed on those of **1**. Therefore **2** is 7-hydroxy-8-γ,γ-dimethylallyl-[6''',6'''-dimethylpyrano (2''',3''':4',3')]flavanone and is named euchrenone a_5.

Compound **3**, $C_{30}H_{34}O_6$, was obtained as a light yellow oil. In the ^1H NMR spectrum, the typical signals based on H-2 and H-3 were observed at δ5.52 (1H, *dd*, *J* = 12.8 and 3.3 Hz), 2.88 (1H, *dd*, *J* = 17.2 and 3.3 Hz), and 3.06 (1H, *dd*, *J* = 17.2 and 12.8 Hz). Further observation indicated the presence of a chromene ring [1.42 (2 × Me), 5.48 and 6.25 (1H each, *d*, *J* = 9.9 Hz, *cis*-olefinic proton)], two γ,γ-dimethylallyl groups [1.72 (2 × Me), 1.75, 1.82 (3H, Me), 3.29, 3.34 (CH_2), 5.16, 5.23 (CH=C<)] and three hydroxyl groups [6.54, 6.57 and 12.31 (chelated)]. Two aromatic protons appearing at δ6.36 and 6.89 as singlets were reasonably assigned to H-3' and H-6'. Furthermore, the chromene ring was fused on B ring, not on the A ring by the chemical shift of *cis*-olefinic proton (δ6.23), which was also indicated by the MS. A fragment ion at *m/z* 187 caused by demethylation of B_1^+ was detected as with euchrestaflavanone C (**6**) [7]. As a result, the B ring moiety has the same substitution pattern as that of **6**. Hence **3** is 5,7,2'-trihydroxy-6,8-di(γ,γ-dimethylallyl)-[6'''',6''''-dimethylpyrano (2'''',3'''':4',3')] flavanone and is named euchrenone a_6.

Both xambioona and euchrenone a_5 are regarded as being derived by oxidative cyclization from glabrol [7,4'-dihydroxy-8,3'-di(γ,γ-dimethylallyl)flavanone], which has been reported as a constituent of *Glycyrrhiza glabra* (roots) [9]. In the present study, a flavanone lacking a hydroxyl group at C-5 was isolated from the genus *Euchresta* for the first time. These flavanones may possibly be characteristic of the species *E. formosana*.

EXPERIMENTAL

Plant material. The roots 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 flavonoids **1**–**7**. Dried roots (700 g) of *E. formosana* were powdered and extracted with CH_2Cl_2, EtOAc and MeOH, successively. The CH_2Cl_2 soln was concd *in vacuo* and subjected to silica gel CC. A fraction eluted by *n*-hexane–EtOAc (30:1–8:1) gave a mixture of **1**–**3**. The mixture was further purified by prep TLC using cyclohexane–EtOAc as eluent to obtain **1** (20 mg), **2** (12 mg) and **3** (10 mg) as pure forms, respectively. From more polar fractions, **4** (200 mg), **5** (22 mg), **6** (120 mg) and **7** (25 mg) were also obtained and identified with the respective authentic samples by direct comparison.

Xambioona (**1**). $C_{25}H_{24}O_4$, M_r 388, a light yellow powder. EIMS (*m/z*) (rel. int.) 388 (32, $[M]^+$), 373 (70, $[M-Me]^+$), 203 (4), 202 (4, $[A_1]^+$), 187 (100, $[A_1-Me]^+$), 186 (10, $[B_1]^+$), 171 (95 $[B_1-Me]^+$). ^1H NMR ($CDCl_3$, 270 MHz): 1.44, 1.45, 1.46, 1.47 (3H, each *br s*, Me), 2.78 (1H, *dd*, *J* = 16.9, 2.9 Hz, H-3), 3.00 (1H, *dd*, *J* = 16.9, 13.2 Hz, H-3), 5.55, 5.64 (1H, each *d*, *J* = 9.9 Hz, H-5'' and H-5'''), 6.33 (1H, *d*, *J* = 9.9 Hz, H-4'''), 6.48 (1H, *d*, *J* = 8.4 Hz, H-6), 6.63 (1H, *d*, *J* = 9.9 Hz, H-4''), 6.89 (1H, *d*, *J* = 8.4 Hz, H-5'), 7.06 (1H, *d*, *J* = 2.2 Hz, H-2'), 7.19 (1H, *dd*, *J* = 8.4, 2.2 Hz, H-6'), 7.73 (1H, *d*, *J* = 8.4 Hz, H-5). UV (MeOH, nm): 267, 312.

Euchrenone a_5 (**2**). $C_{25}H_{26}O_4$, HRMS calc. 390.1831, found 390.1822, a light yellow powder. EIMS (*m/z*) (rel. int.) 390 (33, $[M]^+$), 375 (49, $[M-Me]$), 347 (16, $[M-C_3H_7]$), 335 (5, $[M-C_4H_7]$), 204 (9, $[A_1]^+$), 203 (18), 186 (9, $[B_1]^+$), 176 (9), 171 (100, $[B_1-Me]^+$), 149 (10). ^1H NMR ($CDCl_3$): 1.48 (6H, *br s*, 2 × Me), 1.75 (6H, *br s*, 2 × Me), 2.77 (1H, *dd*, *J* = 16.7, 2.9 Hz, H-3), 3.01 (1H, *dd*, *J* = 16.7, 13.2 Hz, H-3), 3.42 (2H, *br d*, *J* = 7 Hz, CH_2), 5.29 (1H, *br t*, *J* = 7 Hz, CH=C<), 5.35 (1H, *dd*, *J* = 13.2, 2.9 Hz, H-2), 5.65 (1H, *d*, *J* = 9.9 Hz, H-5'''), 6.32 (1H, *d*, *J* = 9.9 Hz, H-4'''), 6.52 (1H, *d*, *J* = 8.4 Hz, H-6), 6.79 (1H, *d*, *J* = 8.4 Hz, H-5'), 7.05 (1H, *d*, *J* = 2.2 Hz, H-2'), 7.15 (1H, *dd*, *J* = 8.4, 2.2 Hz, H-6'), 7.72 (1H, *d*, *J* = 8.4 Hz, H-5). UV (MeOH, nm): 268 sh (3.72), 280 (4.20), 310 sh (3.63).

Euchrenone a_6 (**3**). $C_{30}H_{34}O_6$, HRMS calc. 490.2355, found 490.2349, a light yellow oil. EIMS (*m/z*) (rel. int.) 490 (22, $[M]^+$), 475 $[M-Me]^+$), 472 (45, $[M-H_2O]$), 457 (4), 429 (84), 417 (26), 373 (12), 361 (12), 189 (7), 273 (5), 269 (5), 245 (12), 233 (33), 202 (42, $[B_1]^+$), 187 (100, $[B_1-Me]$). ^1H NMR ($CDCl_3$): 1.42, 1.72 (6H, each *br s*, 2 × Me), 1.75, 1.82 (3H, each *br s*, Me), 2.88 (1H, *dd*, *J* = 17.2, 3.3 Hz, H-3), 3.06 (1H, *dd*, *J* = 17.2, 12.8 Hz, H-3), 3.29, 3.34 (2H, each *br d*, *J* = 7 Hz, CH_2), 5.16, 5.23 (1H, *br t*, *J* = 7 Hz, CH=C<), 5.48 (1H, *d* *J* = 9.9 Hz, H-5''''), 5.52 (1H, *dd*, *J* = 12.8, 3.3 Hz, H-2), 6.25 (1H, *dd*, *J* = 9.9 Hz, H-4''''), 6.36 (1H, *s*, H-3'), 6.40, 6.57 (1H, each *s*, OH), 6.89 (1H, *s*, H-6'), 12.31 (1H, *s*, C_5-OH). UV (MeOH, nm): 294, 347.

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