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CHROMONES AND CHROMANONES FROM *BAECKEA FRUTESCENS*

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Key Word Index—*Baeckea frutescens*; Myrtaceae; dwarf mountain pine; chromones; chromanones.

Abstract—The aerial parts of *Baeckea frutescens* yielded three new chromones (5-hydroxy-7-methoxy-2-isopropyl, 5-hydroxyl-7-methoxy-2-isopropyl-8-methyl and 5-hydroxy-7-methoxy-2-iso-propyl-6-methyl) and five new chromanones (2,5-dihydroxy-7-methoxy-2-isopropyl, 2,5-dihydroxy-7-methoxy-2-isopropyl-8-methyl, 2,5-dihydroxy-7-methoxy-2-isopropyl-6-methyl, 2,5-dihydroxy-7-methoxy-2,8-dimethyl and 2,5-dihydroxy-7-methoxy-2,6-dimethyl). Their structures were deduced from two-dimensional NMR spectroscopy and from comparison of NMR spectra with known chromones, also present in the extract. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Baeckea frutescens L. is an aromatic low-growing shrub widespread in the grasslands of Hong Kong and is used in traditional Chinese medicine for treating rheumatism and snake-bites [1]. Three phloroglucinols have been reported in a very recent phytochemical study of this species [2]. The present paper reports the isolation and structural determination of three new chromones and five new chromanones from the aerial parts of *B. frutescens*.

RESULTS AND DISCUSSION

Extraction of the aerial parts with dichloromethane followed by column chromatography and HPLC yielded two novel chromones (**1** and **2**) in high yield and an isomeric chromone (**3**) in small quantities. Accurate mass spectroscopy demonstrated the elemental composition $C_{13}H_{14}O_4$ for compound **1**. IR revealed the presence of a strongly hydrogen-bonded hydroxyl group (3000 cm^{-1}) and ^{13}C DEPT confirmed the presence of 13 carbons with 13 directly attached protons (Tables 1 and 2). Inspection of the ^{13}C spectrum showed a carbonyl group (δ 182.8), the six carbons of a 1,3,5-oxygenated benzene system (δ 165.4, 162.1, 158.2, 105.4, 97.9 and 92.3) and an enolic double bond (δ 175.0 and 105.9). The presence of an isopropyl group was suggested by the ^1H spectrum (δ 2.83 [1H] *sept* $J = 6.8$ Hz; δ 1.30 [6H] *d*, $J =$ 6.8 Hz) and confirmed by ^1H–^1H COSY. These elements were assembled into the complete structure of a 2-isopropyl-substituted chromone by consideration of single bond (Tables 1 and 2) and long-range ^{13}C–^1H correlation spectra.

The structure of compound **2** ($C_{14}H_{16}O_4$ from high-resolution mass spectrometry) was deduced in the same manner. Compound **2** differed from **1** in that the H-6 proton at δ 6.36 now appeared as a singlet, rather than a doublet (*meta*-coupling $J = 2.2$ Hz) as previously and that a methyl group (δ ^{13}C 7.3; δ ^1H 2.16) appeared in the spectrum, replacing the second *meta*-coupled proton in compound **1**; otherwise, compound **2** gave very similar chemical shifts to compound **1** (Tables 1 and 2). Compound **2** therefore contained an additional aromatic methyl substituent compared with compound **1** and was unambiguously assigned as the 8-methyl analogue of compound **1** by ^{13}C–^1H single-bond and long-range correlation experiments (Fig. 1).

Relatively small amounts of compound **3**, isomeric in the position of the aromatic methyl group, were also isolated in addition to compound **2**. ^{13}C and ^1H chemical shifts for compound **3**, established as previously, were similar to compound **2** and are reported in Tables 1 and 2. Compound **3** was unambiguously identified as the 6-methyl analogue of compound **1** by ^{13}C–^1H single-bond and long-range correlation experiments.

The extract of *B. frutescens* also contained the known compounds **7** and **8**, identified by comparison with NMR spectra and other data reported in the literature [3, 4]. Compounds **7** and **8** are the 2-methyl analogues of the 2-isopropyl chromones **1** and **2**. Complete ^{13}C and ^1H assignments of compounds **7** and **8** were made using the same methodology as described for compounds **1** and **2**; the chemical shift values established for these known compounds thus provided

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Table 1. ^{13}C NMR data for compounds **1**, **2**, **3**, **7** and **8** ($CDCl_3$)

	δ ^{13}C				
Assignment	**1**	**2**	**3**	**7**	**8**
C-2	175.0	174.6	174.4	166.8	166.8
C-3	105.9	105.3	106.0	108.8	108.2
C-4	182.8	183.3	182.8	182.5	183.1
C-5	162.1	160.1	158.4	162.2	160.2
C-6	97.9	94.5	108.7	97.9	94.8
C-7	165.4	162.9	163.3	165.3	163.0
C-8	92.3	103.6	89.2	92.5	103.7
C-9	158.2	154.7	156.4	158.1	155.0
C-10	105.4	104.7	105.2	105.2	104.7
C-11	33.2	33.2	33.2	20.5	20.6
C-12, 13	20.1	20.1	20.1	–	–
6-Me	–	–	7.2	–	–
7 OMe	55.8	55.9	55.9	55.7	56.0
8-Me	–	7.3	–	–	7.4

Table 2. ^{1}H NMR data for compounds **1**, **2**, **3**, **7** and **8** ($CDCl_3$)

	δ ^{1}H				
Assignment	**1**	**2**	**3**	**7**	**8**
H-3	6.02	6.02	6.05	6.02	6.01
H-6	6.28	6.36	–	6.33	6.37
H-8	6.36	–	6.38	6.35	–
H-11	2.83	2.87	2.83	2.35	2.37
H-12, 13	1.30	1.32	1.30	–	–
2-OH	12.71	12.74	12.81	12.69	12.75
6-Me	–	–	2.09	–	–
7-OMe	3.84	3.88	3.90	3.85	3.88
8-Me	–	2.16	–	–	2.15

good evidence for confirming the structure of the novel isopropyl chromones.

Five novel chromanones, **4**, **5a**, **5b**, **6a** and **6b** were also isolated from the extract; compounds **4**, **5a**, **5b** and **6a** can formally be derived from **1**, **2**, **3** and **8**, respectively, by hydration of the 2,3-double bond. The 2-hydroxychromanone **4** gave broadly similar ^{13}C and ^{1}H NMR spectra to those of compound **1**, differing principally in the absence of the alkene resonances (δ

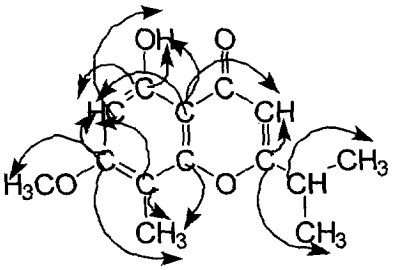
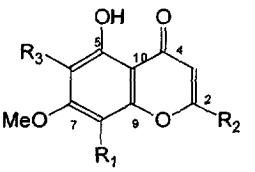
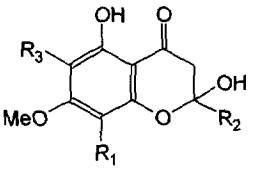


Fig. 1. Long-range ^{13}C–^{1}H correlations for compound **2**.



1 R_1 = H; R_2 = $CH(Me)_2$; R_3 = H
2 R_1 =Me; R_2 = $CH(Me)_2$; R_3 = H
3 R_1 = H; R_2 = $CH(Me)_2$; R_3 = Me
7 R_1 = H; R_2 = Me; R_3 = H
8 R_1 = Me; R_2 = Me; R_3 = H



4 R_1 = H; R_2 =$CH(Me)_2$; R_3 = H
5a R_1 = Me; R_2 =$CH(Me)_2$; R_3 = H
5b R_1 = H; R_2 =$CH(Me)_2$; R_3 = Me
6a R_1 = Me; R_2 =Me; R_3 = H
6b R_1 = H; R_2 =Me; R_3 = Me

^{13}C 175.0, 105.9; δ ^{1}H 6.02), which were replaced by a methylene group (δ ^{13}C 42.1; δ ^{1}H 2.87, *d*, *J* = 17.0 Hz; 2.71, *d*, *J* = 17.0 Hz) and a quaternary carbon bearing two oxygen substituents (δ ^{13}C 104.2). Observation of single bond and long-range ^{13}C–^{1}H correlations allowed assignment of every ^{13}C and ^{1}H resonance in compound **4** (Tables 3 and 4). NOESY showed correlations between the methyl groups of the isopropyl substituent and both protons of the methylene group in the heterocyclic ring, demonstrating that the isopropyl group is equatorial.

Collection of the eluent from two apparently distinct peaks (separated by two minutes) in the HPLC purification of a fraction from column chromatography, of similar polarity to compound **4** yielded two subfractions, both as gums. Both of these, to our surprise, gave identical NMR spectra and appeared to consist of two closely related isomers in a *ca* 1:1 ratio. Through application of high-resolution single-bond and long-range ^{13}C–^{1}H correlation experiments it was possible to separate the ^{1}H and ^{13}C resonances of this mixture into two groups showing mutual correlations within each group, but not between groups. Analysis of correlations for each group led to structures **5a** and **5b** with the assignments shown in Tables 3 and 4. In both cases, high resolution NOESY demonstrated that the 2-isopropyl groups were equatorial.

Further HPLC analysis of each of these subfractions once again demonstrated two peaks with similar retention times as for the original separation in both cases. NMR spectra associated with these two peaks (irrespective of the subfraction used in HPLC) were

Table 3. ^{13}C NMR data for compounds **4–6** ($CDCl_3$)

	δ ^{13}C				
Assignment	**4**	**5a**	**5b**	**6a**	**6b**
C-2	104.2	103.6	104.2	100.3	100.7
C-3	42.1	42.4	42.1	46.7	46.9
C-4	195.2	195.9	195.5	195.3	194.8
C-5	163.8	161.8	160.0	162.1	160.2
C-6	94.87	92.1	105.9	92.3	106.1
C-7	167.9	166.0	165.7	166.1	165.7
C-8	94.92	105.4	91.3	105.3	91.3
C-9	159.7	155.8	158.2	155.8	158.0
C-10	102.6	102.2	102.3	102.2	102.2
C-11	37.8	37.7	37.7	28.5	28.4
C-12, 13	17.0; 16.2	16.9; 16.2	17.0; 16.1	–	–
6-Me	–	–	6.8	–	6.8
7-OMe	55.6	55.8	55.7	55.8	55.8
8-Me	–	7.5	–	7.6	–

once again identical to the original subfraction and to each other. This unexpected result can most simply be explained on the assumption that, although compounds **5a** and **5b** can be separated chromatographically, they are then able to interconvert before or during preparation for NMR spectroscopy *via* the mechanism shown in Fig. 2. The possibility of such tautomerization between hemi-ketal 2-hydroxyflavanones and ring-opened β-ketochalcones has been noted previously [5–11], although we are not aware of such reports for tautomerism of chromanones.

Derivitization of the **5a/5b** mixture with acetic anhydride–pyridine produced a single compound tentatively identified as the ring-opened β-diketone form of the structure **5a/5b** (shown as an intermediate in Fig. 2) with acetylation at both aromatic hydroxyl groups. Derivitization of compounds **5a/5b** with methyl iodide gave a mixture of both *O*- and *C*-methylated products, while dehydration with refluxing sulfuric acid produced a mixture of compounds **2** and **3** in a 1:1 ratio in high yield, as expected.

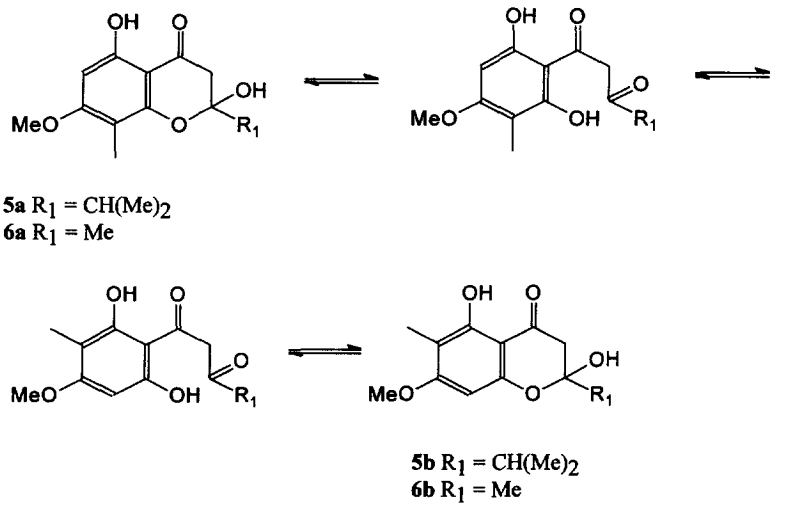
Similar behaviour was observed in the case of compounds **6a** and **6b**, where compound collected from an apparently single HPLC peak, appeared as a 1:1 mixture spectroscopically. Application of high resolution two-dimensional spectra succeeded in establishing the structures **6a** and **6b** from the mixture, with assignments given in Tables 3 and 4 (the 2-methyl substituents were shown to be equatorial in both cases by NOESY). Presumably, compounds **6a** and **6b** are also able to equilibrate with one another by a similar mechanism to that for compounds **5a** and **5b**.

Because of the apparently easy interconversion of 6-methyl and 8-methyl forms of the 2-hydroxychromanones *via* a ring-opened β-keto intermediate, it is not known whether only one isomer or both of the **5a/5b** pair is originally present in the plant. On the assumption that the 2-hydroxychromanones **4** and **5** (present in small quantities) represent biosynthetic intermediates *en route* to the chromones **1** and **2** (isolated in much larger quantities), as shown in Fig. 3, it could be argued that the 8-methyl form **5a** is

Table 4. ^{1}H NMR data for compounds **4–6** ($CDCl_3$)

	δ ^{1}H				
Assignment	**4**	**5a**	**5b**	**6a**	**6b**
H-3	2.87; 2.71	2.82; 2.69	2.83; 2.67	2.91; 2.83	2.93; 2.84
H-6	6.06	6.02	–	6.08	–
H-8	5.97	–	5.98	–	6.01
H-11	2.08	2.13	2.08	–	–
H-12, 13	1.09; 1.07	1.08; 1.07	1.10; 1.06	–	–
2-OH	2.61*	3.38*	3.26*	3.30*	3.30*
2-Me	–	–		1.74	1.72
5-OH	11.94	12.0	11.94	12.04	11.97
6-Me	–	–	1.96	–	1.99
7-OMe	3.80	3.81	3.80	3.84	3.84
8-Me	–	1.95		1.98	–

*Chemical shift variable.



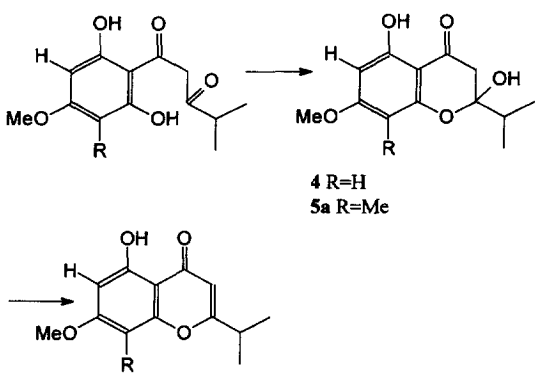
5a $R_1 = CH(Me)_2$
6a $R_1 = Me$

5b $R_1 = CH(Me)_2$
6b $R_1 = Me$

Fig. 2. Interconversion of 6-methyl and 8-methyl chromanones after chromatographic separation.

predominant in the extract. The small amounts of **3** observed might arise from limited isomerization of compound **5a** to **5b** in the plant, the latter then serving as the substrate for subsequent dehydration to compound **3**. Alternatively, both isomers may be present *in vivo* in equilibrium (Fig. 2), with the enzyme involved in dehydration showing a preference for catalysing conversion of the 8-methyl form **5a** to **2**, while only poorly recognizing compound **5b** as a substrate for dehydration to compound **3**.

This is the first report of naturally occurring 2-isopropylchromones, although there has been one previous report concerning a 2-hydroxy-2-isopropylchromanone [12]. 2-Methylchromones are relatively common [13] but no 2-hydroxy-2-methylchromanones have been reported. The known compound sitosterol was also isolated and identified from its NMR spectra [14], in addition to the aforementioned compounds.



4 R=H
5a R=Me

1 R=H
2 R=Me

Fig. 3. Possible biosynthetic route to compounds **1** and **2**.

EXPERIMENTAL

General. Chemical shifts are expressed in δ relative to TMS as int. standard. All NMR expts were run on Bruker DPX 300 or DRX 500 instruments with $CDCl_3$ as solvent. Single-bond and long-range ^{13}C–^{1}H correlation expts were normally recorded with 1024 data points in F_2 and 256 data points in F_1, while high-resolution experiments had 4096 data points in F_2 and 1024 data points in F_1. Mass spectra were recorded in EI mode (70 eV). FTIR spectra were recorded in CH_2Cl_2 or CCl_4. TLC plates were developed using *p*-anisaldehyde. HPLC sepns were performed using a Prep-Sil 20 mm × 25 cm column, flow rate 8 ml min^{-1}.

Isolation of **1–8**. *Baeckea frutescens* L. (*B. chinensis* Gaertner; *B. cochinchinensis* Bl.) (577 g) was collected in November, while flowering from Plover Cove Country Park, New Territories, Hong Kong. A voucher specimen is deposited at the University of Hong Kong Herbarium (GDBROWN 96/1). The sample was ground to a fine powder under liquid N_2 and immediately extracted with CH_2Cl_2 in a Soxhlet apparatus (8 hr). The CH_2Cl_2 extract was then dried and evapd under red. pres. to yield a dark green oil (8.85 g; 1.5% w/w) which was sepd by chromatography. Compound **1** (1.54 g) by CC (R_f 0.34, 20% EtOAc in hexane, staining purple) followed by HPLC (R_t, 14.6 min, 20% EtOAc in hexane); **2** (160 mg) by CC (R_f 0.25, 15% EtOAc in hexane, staining yellow); **3** (12 mg) by CC (R_f 0.21, 10% EtOAc in hexane, staining pale yellow) followed by HPLC (R_t 17.8 min, 14% EtOAc in hexane); **4** (6 mg) by CC (R_f 0.22, 22% EtOAc in hexane; staining pale green) followed by HPLC (R_t 16.3 min, 22% EtOAc in hexane); **5a** and **5b** (67 mg) by CC (R_f 0.28, 22% EtOAc in hexane, staining pale green) followed by HPLC (R_t 16.1 and 18.0 min, respectively, 18% EtOAc in hexane); **6a** and **6b** (13 mg) by CC (R_f 0.24, 35% EtOAC in hexane, staining pale pink) followed by HPLC (R_t 14.3 min,

35% EtOAC in hexane); **7** (10 mg) by CC (R_f 0.13, 22% EtOAc in hexane, staining pale blue) followed by HPLC (R_t 24.9 min, 22% EtOAc in hexane); **8** (30 mg) by CC (R_f 0.24, 20% EtOAc in hexane, staining purple) followed by HPLC (R_t 19.5 mins 20% EtOAc in hexane).

5-*Hydroxy*-7-*methoxy*-2-*isopropylchromone* (**1**). Pale yellow crystals, mp 40–43°. ^{1}H NMR: δ 12.71 (1H, *s*), 6.36 (1H, *d*, J = 2.2 Hz), 6.28 (1H, *d*, J = 2.2 Hz, *d*, J = 2.2 Hz), 6.02 (1H, *s*), 3.84 (3H, *s*), 2.83 (1H, *sept*, J = 6.8 Hz), 1.30 (6H, *d*, J = 6.8 Hz). IR $\nu_{max}^{CH_2Cl_2}$ cm^{-1}: 3000 Br, 2974, 2931, 2879, 2853, 1670 (C=O), 1623, 1585, 1510, 1443. MS *m/z* (rel. int.): 234.0899 (100) ([M]$^+$ Δ0.3 mmu for $C_{13}H_{14}O_4$), 205 (30).

5-*Hydroxy*-7-*methoxy*-2-*isopropyl*-8-*methylchromone* (**2**). Pale yellow crystals, mp 106–109°. ^{1}H NMR: δ 12.74 (1H, *s*), 6.36 (1H, *s*), 6.02 (1H, *s*), 3.88 (3H, *s*), 2.87 (1H, *sept*, J = 6.8 Hz), 2.16 (3H, *s*), 1.32 (6H, *d*, J = 6.8 Hz). nOe irradiation at δ 1.32 produced a small enhancement at δ 6.02; irradiation at δ 3.88 produced a small enhancement at δ 6.36. IR $\nu_{max}^{CH_2Cl_2}$ cm^{-1}: 3000 br, 3010, 2975, 2880, 2935, 2849, 1658 (C=O), 1614, 1588, 1501, 1426. MS *m/z* (rel. int.): 248.1047 (92) ([M]$^+$ Δ0.2 mmu for $C_{14}H_{16}O_4$), 233 (25), 217 (23), 205 (11), 153 (36), 136 (34), 107 (42), 89 (52), 77 (100).

5-*Hydroxy*-7-*methoxy*-2-*isopropyl*-6-*methylchromone* (**3**). Pale yellow crystals mp 100–103°. ^{1}H NMR: δ 12.80 (1H, *s*), 6.38 (1H, *s*), 6.05 (1H, *s*), 3.90 (3H, *s*), 2.85 (1H, *sept*, J = 6.8 Hz), 2.09 (3H, *s*), 1.31 (6H, *d*, J = 6.9 Hz). IR $\nu_{max}^{CH_2Cl_2}$ cm^{-1}: 3000 br, 2964, 2926, 2854, 1659 (C=O), 1628, 1575, 1495, 1410. MS *m/z* (rel. int.): 248.1056 (100) ([M]$^+$ Δ − 0.7 mmu for $C_{14}H_{16}O_4$), 230 (10), 219 (13).

2,5-*Dihydroxy*-7-*methoxy*-2-*isopropylchromanone* (**4**). Pale yellow solid, mp 116–118°. ^{1}H NMR: δ 11.9 (1H, *s*), 6.04 (1H, *d*, J = 2.3 Hz), 5.97 (1H, *d*, J = 2.3 Hz), 3.80 (3H, *s*) 2.87 (1H, *d*, J = 17.0 Hz), 2.71 (1H, *d*, J = 17.0 Hz), 2.08 (1H, *sept* J = 7 Hz), 1.09 (3H, *d*, J = 6.9 Hz), 1.07 (3H, *d*, J = 6.9 Hz). NOESY showed enhancements from δ 1.09 and 1.07 to 2.87, 2.71 and 2.08. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3592, 3430 br, 2962, 2930, 2870, 2860, 1641 (C=O), 1610, 1580, 1520, 1460. MS *m/z* (rel. int.): 252.0994 (8) ([M]$^+$ Δ0.3 mmu for $C_{13}H_{16}O_5$), 233 (8), 209 (100), 167 (47), 107, (9), 89 (9), 77 (20).

2,5-*Dihydroxy*-7-*methoxy*-2-*isopropyl*-8-*methylchromanone and* 2,5-*dihydroxy*-7-*methoxy*-2-*isopropyl*-6-*methylchromanone** (**5a** *and* **5b**). Oil. ^{1}H NMR: δ 12.00 (1H, *s*), 11.94 (1H, *s*)*, 6.02 (1H, *s*), 5.98 (1H, *s*)*,3.81 (3H, *s*), 3.80 (3H, *s*)*, 2.83 (1H, *d*, J = 16.9 Hz)*, 2.82 (1H, *d*, J = 16.9 Hz), 2.69 (1H, *d*, J = 16.9 Hz), 2.67 (1H, *d*, J = 16.9 Hz)*,2.13 (1H, *sept*, J = 6.9 Hz), 2.08 (1H, *sept*, J = 16.9 1.96 (3H, *s*)*, 1.95 (3H, *s*), 1.10 (3H, *s*)*, 1.08 (3H, *d*, J = 6.9 Hz), 1.07 (3H, *d*, J = 6.9 Hz), 1.06 (3H, *s*)*. For **5a**, NOESY showed enhancements from δ 3.81 to 6.02, and from δ 1.08 and 1.07 to 2.82, 2.69 and 2.13. A D_2O shake showed large changes in the ^{13}C NMR at δ 161.8 (+0.280 ppm) and 103.6 (+0.067 ppm) consistent with hydroxylation at positions 5 and 2, respectively. For **5b**, NOESY showed enhancements from δ 3.80 to 5.98, and from δ 1.06 and 1.10 to 2.83 and δ 2.67. A D_2O shake showed large changes in the ^{13}C NMR at δ 160.0 (+0.246 ppm) and 104.2 (+0.069 ppm) consistent with hydroxylation at positions 5 and 2, respectively. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3595, 3420 *br*, 2970, 2930, 2881, 2856, 1640 (C=O), 1587, 1510, 1466, 1449. MS *m/z* (rel. int.): 266.1152 (19) ([M]$^+$ Δ0.2 mmu for $C_{14}H_{18}O_5$), 233 (100), 181 (39).

2,5-*Dihydroxy*-7-*methoxy*-2,8-*dimethylchromanone and* 2,5-*dihydroxy*-7-*methoxy*-2,6-*dimethylchromanone** (**6a** *and* **6b**). Solid, mp 123–125°. ^{1}H NMR: δ 12.04 (1H, *s*), 11.97 (1H, *s*)*, 6.08 (1H, *s*), 6.01 (1H, *s*)*, 3.84 (3H, *s*), 3.84 (3H, *s*)*, 2.93 (1H, *d*, J = 16.9 Hz)*, 2.91 (1H, *d*, J = 16.9 Hz), 2.84 (1H, *d*, J = 16.9 Hz)*, 2.83 (1H, *d*, J = 16.9 Hz), 1.99 (3H, *s*)*, 1.98 (3H, *s*), 1.74 (3H, *s*), 1.72 (3H, *s*)*. NOESY showed enhancement from δ 6.01 and 6.08 to 3.84, from δ 1.74 to 2.91 and 2.83, and from δ 1.72 to 2.93 and 2.84. IR $\nu_{max}^{CCl_4}$: cm^{-1}: 3592, 3420 br, 2937, 2847, 1641 (C=O), 1587, 1510, 1450, 1312. MS *m/z* (rel. int.): 238.0841 (100) ([M]$^+$ Δ0.1 mmu for $C_{12}H_{14}O_5$) 223 (20), 221 (21). 196 (9), 181 (27), 180 (19), 154 (23), 152 (8).

5-*Hydroxy*-7-*methoxy*-2-*methylchromone* (*eugenin*) (**7**). Yellow gum. ^{1}H NMR: δ 12.69 (1H, *s*), 6.35 (1H, *d*, J = 2.3 Hz), 6.33 (1H, *d*, J = 2.3 Hz), 6.02 (1H, *s*), 3.85 (3H, *s*), 2.35 (3H, *s*). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3359 br, 2961, 2932, 2872, 1661 (C=O), 1628, 1600, 1506, 1450, 1414, 1384, 1342. MS *m/z* (rel. int.): 206.0578 (100 [M]$^+$ Δ0.1 mmu for $C_{11}H_{10}O_4$) 181 (39), 177 (19).

5-*Hydroxy*-7-*methoxy*-2,8-*dimethylchromone* (*iso-eugenitin*) (**8**). Gum. ^{1}H NMR: δ 12.75 (1H, *s*), 6.37 (1H, *s*), 6.01 (1H, *s*), 3.89 (3H, *s*), 2.37 (3H, *s*), 2.15 (3H, *s*). IR $\nu_{max}^{CH_2Cl_2}$ cm^{-1}: 3400 br, 2928, 2854, 1662 (C=O), 1615, 1598, 1510, 1420, 1394. MS *m/z* (rel. int.): 220.0731 (100 [M]$^+$ Δ0.4 mmu for $C_{12}H_{12}O_4$), 189 (15), 153 (18), 136 (13).

Conversion of **5a/5b** *to* **2/3**. The 1:1 mixt. of **5a/5b** (10 mg) was refluxed in 20% H_2SO_4 (2 hr) [15]. Compounds **2** and **3** were isolated as a 1:1 mixt. (8 mg) upon work-up, with no need for further purification.

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