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J. Nat. Prod., **1994**, 57 (5), 673-676 • DOI:
10.1021/np50107a021 • Publication Date (Web): 01 July 2004

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DC 20036

FARNESYL ACETOPHENONE AND FLAVANONE COMPOUNDS FROM THE AERIAL PARTS OF *BORONIA RAMOSA*

MONIRA AHSAN, ALEXANDER I. GRAY, PETER G. WATERMAN,*

Phytochemistry Research Laboratories, Department of Pharmaceutical Sciences,
University of Strathclyde, Glasgow, G1 1XW, UK

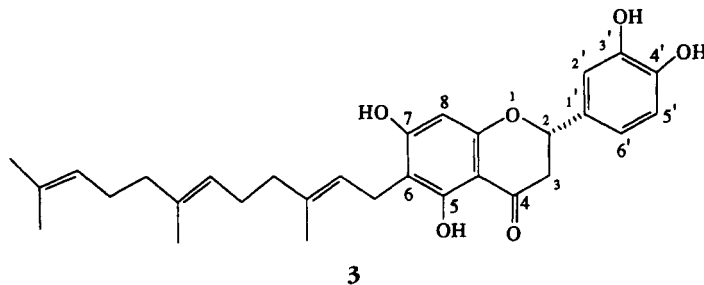
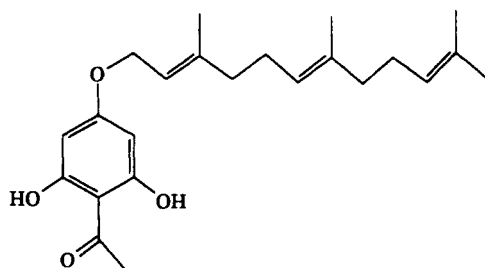
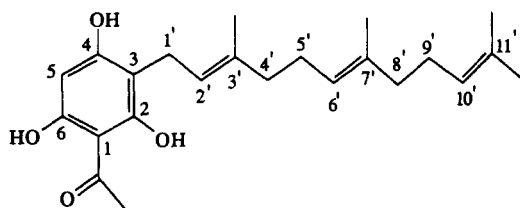
and JAMES A. ARMSTRONG¹

Western Australian Herbarium, Department of Conservation and Land Management,
Como, Western Australia, Australia 6052

ABSTRACT.—The novel compounds 3-farnesyl-2,4,6-trihydroxyacetophenone [**1**], 4-farnesyloxy-2,6-dihydroxyacetophenone [**2**], and 6-farnesyl-3',4',5,7-tetrahydroxyflavanone [**3**] have been isolated from the aerial parts of *Boronia ramosa* and identified by spectroscopic analysis.

The secondary metabolites of the large Australian genus *Boronia* (Rutaceae) (1) have been little studied. The previ-

ously uninvestigated *Boronia ramosa* (Lindl.) Benth. is restricted in distribution to the south-west part of Western



¹Current Address: Department of Conservation and Land Management, Hackett Drive, Crawley, Perth, Western Australia, Australia 6009.

TABLE 1. ^1H - and ^{13}C -Nmr Chemical Shift Data for Compounds **1** and **2**.^a

Position	Compound			
	δ_{H}		δ_{C}	
	1	2	1	2
C-1			105.4	105.3
C-2			160.7 ^b	163.6 ^b
C-3		5.95 s	105.7	95.0
C-4			161.6 ^b	165.4 ^b
C-5	5.88 s	5.95 s	95.5	95.0
C-6			162.6 ^b	163.6 ^b
C=O			204.1	203.7
CH ₃	2.68 s	2.69 s	33.0	32.9
C-1'	3.37 d (7.0)	4.52 d (6.6)	21.7	65.4
C-2'	5.26 t (7.0)	5.44 t (6.6)	121.6	118.6
C-3'			140.2	142.5
3'-CH ₃	1.78 s	1.73 s	16.5	16.9
C-4'	1.94–2.16 m	1.94–2.16 m	39.9	39.7
C-5'	1.94–2.16 m	1.94–2.16 m	26.5 ^c	26.3 ^c
C-6'	5.08 t (6.6)	5.09 t (6.6)	123.7	123.7
C-7'			135.9	135.8
7'-CH ₃	1.60 s	1.60 s	16.3	16.2
C-8'	1.94–2.16 m	1.94–2.16 m	39.9	39.9
C-9'	1.94–2.16 m	1.94–2.16 m	26.9 ^c	26.9 ^c
C-10'	5.08 t (6.6)	5.09 t (6.6)	124.5	124.5
C-11'			131.5	131.6
11'-CH ₃	1.68 s	1.68 s	25.9	25.9
	1.60 s	1.60 s	17.9	17.9

^aSpectra run in CDCl₃; *J* values (Hz) in parentheses.

^{b,c}Assignments with the same superscript are interchangeable.

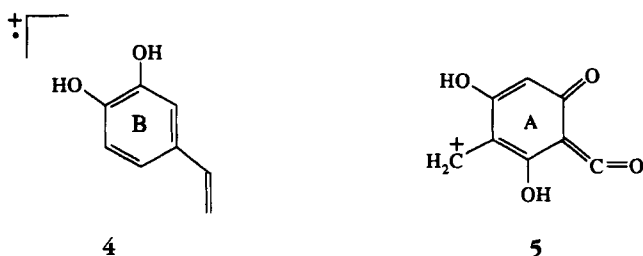
Australia (**1**). In this paper we report the isolation and identification from this species of two novel acetophenones and a novel flavanone, each of which possesses either a *C*-farnesyl or *O*-farnesyl moiety.

The three novel compounds were isolated from a petroleum ether extract by vlc followed by prep. tlc. All three compounds gave similar uv spectra, with a major band at 284–290 nm and a shoulder at 321–334 nm. This is typical of flavanone and acetophenone systems (2–4).

The hreims of **1** revealed the molecular ion at *m/z* 372 (C₂₃H₃₂O₄). The major ion at *m/z* 181 [C₉H₉O₄]⁺ indicated the loss of [C₁₄H₂₃]⁺, typical of fission between C-1' and C-2' of a *C*-farnesyl side-chain. The presence of a *C*-farnesyl substituent was confirmed by the ^1H -nmr spectrum (Table 1). Other signals in the ^1H -nmr spectrum could be assigned to a

single aromatic proton and an acetyl methyl, typical of an acetophenone (**5**). The ^{13}C -nmr spectrum (Table 1) resolved all 23 carbons, which were attributable to the farnesyl group and a 2,4,6-oxygenated acetophenone. Given the phloroglucinol-type oxygenation pattern (obvious from the ^{13}C -nmr spectrum), **1** could be unequivocally identified as 3-farnesyl-2,4,6-trihydroxyacetophenone.

The hreims of **2** showed an identical molecular ion to **1**, but a major ion at *m/z* 168 [C₈H₈O₄]⁺ required the loss of the entire farnesyl moiety, and suggested an *O*-farnesyl substituent. This was confirmed by the ^1H -nmr spectrum (Table 1), which now exhibited two equivalent aromatic protons and deshielding of the 1'-methylene protons due to bonding to oxygen. Since both the ^1H - and ^{13}C -nmr spectra (Table 1) indicated that the acetophenone ring is symmetrical, the

FIGURE 1. Diagnostic Fragment Ions in the Ms of **3**.

farnesyl substituent must be placed at C-4, so that **2** was identified as 4-farnesyloxy-2,6-dihydroxyacetophenone.

Compound **3** revealed a molecular ion at m/z 492 ($C_{30}H_{36}O_6$ by hreims), with a base peak at m/z 301 due to loss of the farnesyl-derived $[C_{14}H_{23}]^+$ ion (cf. **1**). Other ions at m/z 136 [**4**] and m/z 165 [**5**] (Figure 1) were, respectively, suggestive of a flavanone with two hydroxyl groups in ring B and a 5,7-dioxygenated ring A that also carried the remaining one-carbon unit left after fission of the C-farnesyl unit (2). The 1H -nmr spectrum (Table 2) revealed the H-bonded 5-OH, a single A-ring aromatic proton, three B-ring protons with an ABD spin-system, the ABX system of a flavanone C ring and the signals for a C-farnesyl side-chain. The ^{13}C -nmr spectrum (Table 2) was in agreement with these findings. The remaining problems of placement of the farnesyl unit at C-6 or C-8 and unequivocal assignment of carbon resonances were resolved by means of an HMBC nmr study (6). The critical observations were the 3J interaction between the 5-OH proton and the quaternary carbon at 107.6 ppm, and the 2J interaction between the H_2 -1" protons and the same carbon. This carbon must be assigned to C-6 and this established the structure of **3** as 6-farnesyl-3',4',5,7-tetrahydroxyflavanone.

This appears to be the first record of farnesyl acetophenone derivatives in the Rutaceae (7).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv, Perkin-Elmer 552 in MeOH; ir, Perkin-Elmer

781 KBr disks; specific rotations, $[\alpha]_D$, Perkin-Elmer 241; nmr, Bruker AMX-400 (1H , 400 MHz; ^{13}C , 100.6 MHz) all pulse sequences used modified Bruker microprograms; eims, AEI-MS902 double-focusing at 70 eV. Melting points (uncorrected, Reichert hot-stage). Petroleum ether refers to the bp 60–80° fraction.

TABLE 2. 1H - and ^{13}C -Nmr Chemical Shift Data for Compound **3**.^a

Position	δ_H	δ_C
C-2	5.20 dd (12.8, 2.8)	78.9
C-3	2.72 dd (16.8, 2.8); 2.99 dd (16.8, 12.8)	43.3
C-4		196.6
C-4a		103.0
C-5	12.27 s	161.5
C-6		107.6
C-7		164.4
C-8	5.96 s	95.9
C-8a		161.2
C-1'		131.4
C-2'	6.93 d (2.0)	113.8
C-3'		144.1
C-4'		144.4
C-5'	6.84 d (8.0)	115.8
C-6'	6.79 dd (8.0, 2.0)	119.4
C-1''	3.33 d (7.0)	21.3
C-2''	5.25 t (7.0)	121.5
C-3''		139.2
3''-CH ₃	1.80 s	16.5
C-4''	1.95–2.12 m	39.9
C-5''	1.95–2.12 m	26.6 ^b
C-6''	5.06 t (6.6)	123.9
C-7''		135.8
7''-CH ₃	1.59 s	16.3
C-8''	1.95–2.12 m	39.9
C-9''	1.95–2.12 m	26.9 ^b
C-10''	5.07 t (6.6)	124.6
C-11''		131.5
11''-CH ₃	1.67 s	25.9
	1.60 s	17.9

^aSpectra run in $CDCl_3$; J values (Hz) in parentheses.

^bAssignments are interchangeable.

PLANT MATERIAL.—*Boronia ramosa* was collected in a sand heath, about 25 km west of Three Springs, which is north-east of Eneabba (some 270 km north east of Perth, Western Australia, Australia) and a voucher (PERTH 01164333) has been deposited at the Western Australian Herbarium, Perth, Australia.

EXTRACTION AND ISOLATION.—The ground aerial parts (95 g) were extracted sequentially in a Soxhlet with petroleum ether, EtOAc, and MeOH. The concentrated petroleum ether extract was fractionated by vlc over Si gel eluting with petroleum ether containing increasing amounts of EtOAc. Elution with 35–50% EtOAc yielded a mixture of **1**–**3**. Prep. tlc of the mixture on Si gel, with multiple development using 10% EtOAc in petroleum ether gave **1** (18 mg), **2** (13 mg), and **3** (15 mg).

3-Farnesyl-2,4,6-trihydroxyacetophenone [**1**].—Amorphous solid, mp 112–115°; uv λ max (log ϵ) 290 (4.27), 327 (3.52) nm; ir ν max 3420, 3330, 2960, 2920, 2850, 1640, 1630, 1595, 1560, 1450, 1435, 1400, 1370, 1285, 1235, 1150, 1070, 815 cm^{-1} ; ^1H and ^{13}C nmr, see Table 1; eims m/z M^+ 372.2314 (calcd for $\text{C}_{23}\text{H}_{32}\text{O}_4$ 372.2301) (100), 235 (23), 219 (47), 181 (53), 95 (58).

4-Farnesyloxy-2,6-dihydroxyacetophenone [**2**].—Gum; uv λ max (log ϵ) 284 (4.36), 321 (3.57) nm; ir ν max 3140, 2960, 2910, 2840, 1660, 1635, 1585, 1550, 1530, 1440, 1365, 1300, 1255, 1220, 1165, 1070, 950, 825, 800 cm^{-1} ; ^1H and ^{13}C nmr, see Table 1; eims m/z 372.2314 (calcd for $\text{C}_{23}\text{H}_{32}\text{O}_4$ 372.2301) (9), 204 (14), 168 (42), 153 (58), 137 (12), 123 (9), 121 (13), 119 (10), 95 (11), 93 (28), 81 (42), 69 (100).

6-Farnesyl-3',4',5,7-tetrahydroxyflavanone [**3**].—Gum; $[\alpha]_D -24^\circ$ ($c=1.0$, CHCl_3); uv λ max (log ϵ) 290 (4.25), 334 (3.53) nm; ir ν max

3300, 2960, 2910, 2840, 1640, 1630, 1600, 1450, 1340, 1300, 1280, 1160, 1085, 815, 780 cm^{-1} ; ^1H and ^{13}C nmr, see Table 2; eims m/z 492.2523 (calcd for $\text{C}_{30}\text{H}_{36}\text{O}_6$, 492.2512) (9), 355 (6), 339 (12), 301 (100), 219 (75), 203 (12), 191 (6), 177 (7), 165 (61), 136 (9), 81 (17), 69 (41).

ACKNOWLEDGMENTS

One of us (M.A.) thanks the Association of Commonwealth Universities for the award of a Fellowship. We are grateful to Mr. Ray Cranfield for making the collection of plant material used in this study. Nmr experiments were performed in the Nmr Laboratory of the University of Strathclyde. P.G.W. acknowledges the support of the Royal Society and the Carnegie Trust for the Universities of Scotland.

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Received 9 December 1993