

**4-Quinolinone, 2-Quinolinone, 9-Acridanone,  
and Furoquinoline Alkaloids from  
the Aerial Parts of *Boronia bowmanii***

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OF *BORONIA BOWMANII*

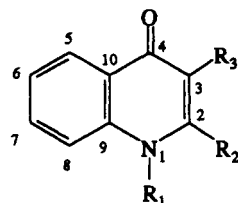
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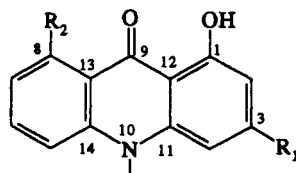
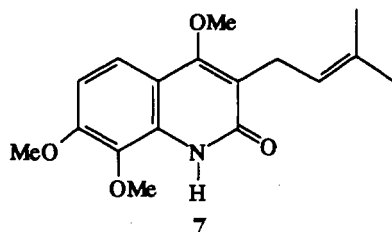
ABSTRACT.—Thirteen alkaloids have been isolated from the aerial parts of *Boronia bowmanii* (Rutaceae). These were identified on the basis of spectroscopic analysis as 1-acetoxymethyl-2,3-dimethyl-4-quinolinone, 1-acetoxymethyl-2-methyl-4-quinolinone, 2,3-dimethyl-4-quinolinone, 1-acetoxymethyl-2-nonyl-4-quinolinone [4], 1-methyl-2-nonyl-4-quinolinone, 2-nonyl-4-quinolinone, 1-hydroxy-9-acridanone, 1,8-dihydroxy-9-acridanone, 1,8-dihydroxy-3-methoxy-9-acridanone [10], preskimmianine, dictamnine, evolitrine, and  $\gamma$ -fagarine. Alkaloids 4 and 10 are novel.

In a recent paper (1) we reported the occurrence of a number of novel 4-quinolinone and acridone alkaloids from *Boronia lanceolata* F. Muell. (Rutaceae), a species found in Northern Australia. Several of the quinolinone alkaloids had an unusual *N*-acetoxymethyl substituent that had previously been reported from *Boronia ternata* Endl. (2), a species found in southwestern Australia and at that point the only other recorded source of alkaloids in the genus. Continuing our studies on *Boronia* we have now undertaken an examination of a sample of *B. bowmanii* F. Muell., which occurs in north-eastern Australia (3). This species, which had not previously been investigated, has also been found to be a good source of 4-quinolinone and, to a lesser extent, acridone and furoquinoline alkaloids.

The petroleum ether extract of *B. bowmanii* afforded thirteen alkaloids, six 4-quinolinones [1–6], a 2-quinolinone [7], three 9-acridanones [8–10], and three furoquinolines [11–13]. Of these 1, 2, 3, 8, and 9 had previously been isolated

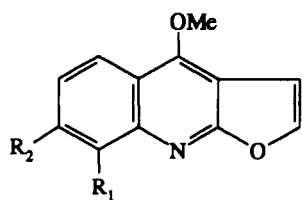


	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1	CH <sub>2</sub> OAc	Me	Me
2	CH <sub>2</sub> OAc	Me	H
3	H	Me	Me
4	CH <sub>2</sub> OAc	<i>n</i> -nonyl	H
5	Me	<i>n</i> -nonyl	H
6	H	<i>n</i> -nonyl	H



	R <sub>1</sub>	R <sub>2</sub>
8	H	H
9	H	OH
10	OMe	OH

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	R <sub>1</sub>	R <sub>2</sub>
<b>11</b>	H	H
<b>12</b>	H	OMe
<b>13</b>	OMe	H

from *B. lanceolata* (1), and their identity was established by co-tlc and comparison of uv and <sup>1</sup>H-nmr data with values already published. Compounds **5** (4,5), **6** (5), **7** (6), **11** (7), **12** (8), and **13** (7,8) were identified by comparison with literature data.

The hreims of **4** revealed the molecular ion at *m/z* 343 (C<sub>21</sub>H<sub>29</sub>NO<sub>3</sub>). The <sup>1</sup>H-nmr spectrum (Table 1) was similar to that of the known compound **2**, revealing four aromatic proton multiplets comprising an ABCD system, an isolated aromatic proton and methylene and acetoxy resonances typical of an *N*-acetoxy methyl moiety. Additional signals for a deshielded methylene, seven further methylenes, and a methyl suggested an *n*-nonyl substituent, comparable to that found in **5** and **6** (4,5). A *J*-modulated

TABLE 1. <sup>1</sup>H and <sup>13</sup>C-Nmr Chemical Shift Data for Compound **4**.<sup>a</sup>

Position	δ <sub>H</sub>	δ <sub>C</sub>
2		154.4
3	6.20 s	112.0
4		178.5
5	8.38 dd (8.0, 1.5)	126.9
6	7.36 dd (8.0, 7.2)	124.1
7	7.64 ddd (8.6, 7.2, 1.5)	132.6
8	7.49 d (8.6)	115.5
9		141.4
10		126.4
1'	6.13 s	68.9
2'		170.1
3'	2.12 s	20.9
1"-8"	2.74 t (7.6)	22.8-33.6
	1.67 m	
	1.26-1.46 m	
9"	0.87 t (6.8)	14.2

<sup>a</sup>Spectra run in CDCl<sub>3</sub>, and *J* values are shown in parentheses.

<sup>13</sup>C-nmr spectrum (Table 1) was in agreement with that expected for **4**.

The hreims of **10** displayed a base peak at *m/z* 257, corresponding to the molecular formula C<sub>14</sub>H<sub>11</sub>NO<sub>4</sub>. The <sup>1</sup>H-nmr spectrum (Table 2) revealed five aromatic protons, two of which exhibited only meta-coupling and could be attributed to H-2 and H-4. The three remaining aromatic protons were in an ABC spin-system suggesting placement at H-5, H-6, and H-7. Other signals were a 3H singlet, which could be due to either an *O*-methyl or an *N*-methyl substituent and two chelated OH resonances. The *J*-modulated <sup>13</sup>C-nmr spectrum (Table 2) confirmed the presence of a methoxy group. These data allowed the identification of **10** as 1,8-dihydroxy-3-methoxy-9-acridanone.

TABLE 2. <sup>1</sup>H and <sup>13</sup>C-Nmr Chemical Shift Data for Compound **10**.<sup>a</sup>

Position	δ <sub>H</sub>	δ <sub>C</sub>
1	13.44 s <sup>a</sup> (OH)	167.2
2	6.54 d (2.2)	96.3
3		164.5
4	6.48 d (2.2)	90.3
5	6.96 d (8.4)	106.6
6	7.52 dd (8.4, 8.0)	136.6
7	6.81 d (8.0)	107.6
8	13.34 s <sup>a</sup> (OH)	162.8
9		185.1
10	13.02 br s	
11		144.9
12		104.6
13		108.8
14		143.3
OMe	3.69 s	56.0

<sup>a</sup>Assignments within a column are interchangeable; spectra were run in pyridine-*d*<sub>5</sub>.

The alkaloid profile exhibited by *B. bowmanii* is very similar to that of *B. lanceolata* (1). 4-Quinolinone alkaloids with the unusual *N*-acetoxy methyl substituent have now been identified in all three *Boronia* species from which alkaloids have been isolated. Otherwise this substituent is known from only two other sources in the Rutaceae, *Eriostemon australasius* ssp. *banksii* (9), which is itself closely allied to *Boronia* (10), and in

*Zanthoxylum* (11). A further striking metabolic convergence is the co-occurrence of these 2-alkyl-4-quinolinones and simple acridones in the Eurasian species *Ruta graveolens* (4,12).

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv (Perkin-Elmer 552) in MeOH; ir (Perkin-Elmer 781) KBr disks; specific rotations (Perkin-Elmer 241); nmr Bruker AMX-400 ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 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.

PLANT MATERIAL.—*Boronia boumanii* was collected from Cape York Peninsula, in the far north of Queensland, Australia, and a voucher specimen has been deposited at the Western Australian Herbarium, Perth (PERTH 01734091).

EXTRACTION AND ISOLATION.—The ground aerial parts (280 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 50–60% EtOAc yielded a mixture of **8**, **9**, and **10**. These were purified by cc using Sephadex LH-20 to give **8** [2 mg, mp 255°; lit. (1) 252–254°]. Compounds **9** and **10** were separated by prep. tlc on Si gel, with multiple development using CHCl<sub>3</sub> to give **9** [4.5 mg, mp 252°; lit. (1) 250°] and **10** (2 mg). Elution with 70–80% EtOAc gave **11** [1.4 mg, mp 132°; lit. (4) 129–132°], **12** (3 mg, mp 114°; lit. (13) 114–115°), **13** (1.5 mg, mp 140°; lit. (14) 141–142°), **4** (35 mg), and **7** (2 mg, mp 154°; lit. (6) 151–152°), which were also separated by cc over Sephadex and then prep. tlc on Si gel [multiple development with toluene-EtOAc (17:3)]. Elution with EtOAc alone yielded **1** [50 mg, mp 174°; lit. (1) 175–178°].

Vlc of the EtOAc extract over Si gel afforded, on elution with 5–20% MeOH in EtOAc, a mixture of alkaloids. On concentration of the eluate **3** [100 mg, mp 314–317°; lit. (1) 310–315°] crystallized out. Passage of the supernatant through a Sephadex LH-20 column followed by prep. tlc over Si gel [solvent: CHCl<sub>3</sub>-MeOH (98:2) multiple development] gave **2** [1 mg, mp 162°; lit. (1) 160–164°], **5** [15 mg, mp 75°; lit. (5) 74–76°] and **6** [45 mg, mp 135°; lit. (15) 138–139°].

1-Acetoxyethyl-2-nonyl-4-quinolinone [**4**].—Amorphous solid, mp 79°; uv  $\lambda$  max (log  $\epsilon$ ) 234 (4.13), 313 (3.82), 326 (3.87) nm; ir  $\nu$  max 2920, 2840, 1740, 1630, 1600, 1585, 1485, 1470, 1420, 1380, 1300, 1245, 1210, 1200, 1150, 1075, 1020,

955, 845, 760 cm<sup>-1</sup>;  $^1\text{H}$  and  $^{13}\text{C}$  nmr see Table 1; eims  $m/z$  M<sup>+</sup> 343.2134 (calcd for C<sub>21</sub>H<sub>29</sub>NO<sub>3</sub>, 343.2147) (67), 329 (15), 314 (24), 300 (70), 298 (11), 286 (19), 284 (53), 270 (23), 258 (18), 244 (71), 231 (87), 214 (10), 202 (11), 198 (11), 188 (78), 186 (21), 184 (19), 172 (54), 159 (100), 144 (9), 132 (8), 130 (21), 77 (10).

1,8-Dihydroxy-3-methoxy-9-acridanone [**10**].—Yellow needles from CHCl<sub>3</sub>, mp 275°; uv  $\lambda$  max (log  $\epsilon$ ) 253 (4.35), 271 (4.23), 306 (3.81), 311 (3.83), 325 (3.60), 397 (3.40) nm; ir  $\nu$  max 3300, 1665, 1645, 1605, 1490, 1355, 1285, 1235, 1200, 1160, 1110, 825, 760 cm<sup>-1</sup>;  $^1\text{H}$  and  $^{13}\text{C}$  nmr see Table 2; eims  $m/z$  M<sup>+</sup> 257.0691 (calcd for C<sub>14</sub>H<sub>11</sub>NO<sub>4</sub>, 257.0688) (100), 228 (54), 214 (11), 199 (16), 186 (15), 140 (10), 128 (6), 114 (15), 95 (13).

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## LITERATURE CITED

1. M. Ahsan, A.I. Gray, G. Leech, and P.G. Waterman, *Phytochemistry*, **33**, 1507 (1993).
2. A.M. Duffield and P.R. Jefferies, *Aust. J. Chem.*, **16**, 292 (1963).
3. R.W. Elliot and D.L. Jones, "Encyclopaedia of Australian Plants Suitable for Cultivation," Lothian Publishing Company, Sydney, 1982, Vol. 2, p. 337.
4. M.F. Grundon and H.M. Okely, *Phytochemistry*, **18**, 1768 (1979).
5. R. Somanathan and K.M. Smith, *J. Heterocyclic Chem.*, **18**, 1077 (1981).
6. R. Storer and D.W. Young, *Tetrahedron*, **29**, 1217 (1973).
7. M.F. Grundon and N.J. McCorkindale, *J. Chem. Soc.*, 2177 (1957).
8. N.S. Narashimhan and R.S. Mali, *Tetrahedron*, **30**, 4153 (1974).
9. E.V.L. da Cunha, J.A. Armstrong, A.I. Gray, D.R. Hockless, P.G. Waterman, and A. White, *Aust. J. Chem.*, **46**, 1507 (1993).
10. P.G. Wilson, *Nuytsia*, **1**, 4 (1970).
11. F.R. Stermitz and I.A. Sharifi, *Phytochemistry*, **16**, 2003 (1977).
12. J. Reisch, Z. Rozsa, K. Szendrei, and J. Korosi, *Phytochemistry*, **14**, 1840 (1975).
13. R.G. Cooke and A.F. Haynes, *Aust. J. Chem.*, **7**, 273 (1954).
14. J.F. Collins, G.A. Gray, M.F. Grundon, D.M. Harrison, and C.G. Spyropoulos, *J. Chem. Soc., Perkin Trans. I*, 94 (1973).
15. I.C. Wells, *J. Biol. Chem.*, **196**, 331 (1952).

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