

## CHEMISTRY OF ACRONYCINE IV. MINOR CONSTITUENTS OF ACRONINE AND THE PHYTOCHEMISTRY OF THE GENUS *ACRONYCHIA*<sup>1</sup>

SHINJI FUNAYAMA and GEOFFREY A. CORDELL

Program for Collaborative Research in the Pharmaceutical Sciences, College of Pharmacy,  
University of Illinois at Chicago, Chicago, IL 60612

**ABSTRACT.**—In the course of isolating acronycine (**1**) from an alkaloid fraction of the bark of *Acronychia baueri* (Rutaceae), five alkaloids, 1,2,3-trimethoxy-10-methyl-acridone (**9**), 1,3,4-trimethoxy-10-methyl-acridone (**10**), des-*N*-methyl acronycine (**14**), normelicopine (**5**), and noracronycine (**2**), were isolated. Four of the isolates are new to the genus, and a phytochemical analysis of the genus *Acronychia* is presented.

*Acronychia baueri* Schott (Rutaceae) is the source of the potent antineoplastic alkaloid acronycine (**1**) (1,2). In previous reports from this laboratory, we have described the cmr spectra of acronycine and some derivatives (3), the dimerization of noracronycine (**2**) (4), the trimerization of **2** (5), and the pmr spectra of acronycine and its derivatives (6). During the course of isolating large quantities of acronycine for chemical evaluation, a number of alkaloids were also obtained, and these are the subject of this present report. A brief review of the phytochemistry of the genus *Acronychia* is presented in Table 1 (7-15) which summarizes the isolation of alkaloids from *Acronychia* species, classified according to structure, and Table 2 (6-25) which indicates the miscellaneous compounds that have been obtained.

Successive chromatography of the alkaloid mixture from the bark of *A. baueri* on alumina and/or silica gel followed by repeated preparative tlc gave 1,2,3-trimethoxy-10-methyl-acridone (**9**), 1,3,4-trimethoxy-10-methyl-acridone (**10**), des-*N*-methyl acronycine (**14**), normelicopine (**5**), and noracronycine (**2**).

The uv spectrum of 1,2,3-trimethoxy-10-methyl acridone (**9**) indicated it to be an acrid-9-one alkaloid, and the mass spectrum revealed a molecular ion at  $m/z$  299. In the pmr spectrum, three methoxyl signals and an *N*-methyl signal ( $\delta$  4.046, 4.035, 3.927, and 3.851) were observed, together with four coupled aromatic protons and a singlet proton at  $\delta$  6.627. The most downfield proton ( $\delta$  8.513, dd,  $J = 1.6, 8.0$  Hz) is attributed to the C8-H, thereby establishing a C1-OCH<sub>3</sub>. Comparison with the chemical shift of C4-H (or its equivalent) in a variety of acridone alkaloids (4,6,26,27) indicated that these protons resonate in the region  $\delta$  6.23-6.38. However, comparison with the data for 1,2,3-trimethoxy-10-methyl acridone (**9**) (28) indicated that this compound also exhibited a singlet aromatic proton at  $\delta$  6.56. An unambiguous distinction between the 1,2,3-trimethoxy- and 1,2,4-trimethoxy-10-methyl acridone isomers was made on the basis of transient nOe experiments at 360 MHz. Irradiation of H-5 ( $\delta$  7.448) caused a 1.5% enhancement in the signal at  $\delta$  3.851, thereby demonstrating this to be the 10-methyl resonance. As expected, irradiation of the singlet at  $\delta$  6.627 (H-3 or H-4) caused enhancement in two of the three-proton singlets ( $\delta$  4.035 and 3.851). Since the latter singlet was also affected by irradiation at H-5, the singlet aromatic proton must be at H-4, not at H-2 or H-3, and the isolate has the structure **9**.

1,2,3-Trimethoxy-10-methyl acridone (**9**) was first synthesized by Hughes and co-workers (29,30) and subsequently isolated from *Vepris bilocularis* (31) and *Melicope leratii* (28), both in the family Rutaceae. It is reported from the genus *Acronychia* for the first time.

The uv spectrum of 1,3,4-trimethoxy-10-methyl acridone (**10**) revealed it to be an

<sup>1</sup>For paper III in this series, see reference 5.

TABLE 1. Alkaloids Isolated from *Acronychia* Species

Compound	Plant	Plant part <sup>a</sup>	Reference
<b>Acridone alkaloids</b>			
1,3-dimethoxy-10-methyl acridone ( <b>3</b> ) . . . . .	<i>Acronychia baueri</i>	lf	7
2,3-dimethoxy-1-hydroxy-10-methyl acridone ( <b>4</b> ) . . . . .	<i>A. haplophylla</i> (F.v. Muell.) Engl.	lf	8
normelicopine ( <b>5</b> ) . . . . .	<i>A. baueri</i>	bk	9,b
normelicopidine ( <b>6</b> ) . . . . .	<i>A. baueri</i>	bk	2,9
xanthevodine ( <b>7</b> ) . . . . .	<i>A. baueri</i>	lf	10
melicopine ( <b>8</b> ) . . . . .	<i>A. baueri</i>	bk	2,9,11,12
	<i>A. baueri</i>	lf	7
1,2,3-trimethoxy-10-methyl acridone ( <b>9</b> ) . . . . .	<i>A. baueri</i>	bk	b
1,3,4-trimethoxy-10-methylacridone ( <b>10</b> ) . . . . .	<i>A. baueri</i>	bk	b
melicopidine ( <b>11</b> ) . . . . .	<i>A. baueri</i>	bk	9,11,12
	<i>A. baueri</i>	lf	7
normelicopicine ( <b>12</b> ) . . . . .	<i>A. baueri</i>	bk	9
melicopicine ( <b>13</b> ) . . . . .	<i>A. baueri</i>	bk	9,13
	<i>A. baueri</i>	lf	7,11,12
<b>Prenylacridone alkaloids</b>			
acronycine ( <b>1</b> ) . . . . .	<i>A. baueri</i>	bk	2,9,11,12
des- <i>N</i> -methyl acronycine ( <b>14</b> ) . . . . .	<i>A. baueri</i>	bk	b
noracronycine ( <b>2</b> ) . . . . .	<i>A. baueri</i>	bk	b
acronidine ( <b>15</b> ) . . . . .	<i>A. baueri</i>	lf	7
acrophylline ( <b>16</b> ) . . . . .	<i>A. haplophylla</i>	bk	14
	<i>A. haplophylla</i>	lf	8
acrophyllidine ( <b>17</b> ) . . . . .	<i>A. haplophylla</i>	bk	14
	<i>A. haplophylla</i>	lf	8
<b>Quinoline alkaloids</b>			
1,2-dimethyl-quinol-4-one ( <b>18</b> ) . . . . .	<i>A. baueri</i>	lf	10
<b>Furoquinoline alkaloids</b>			
acronycidine ( <b>19</b> ) . . . . .	<i>A. baueri</i>	bk	9,11,12
	<i>A. baueri</i>	lf	7
evolitrine ( <b>20</b> ) . . . . .	<i>A. pedunculata</i> (L.) Miq.	wd	15
kokusaginine ( <b>21</b> ) . . . . .	<i>A. baueri</i>	lf	7
	<i>A. pedunculata</i>	lf	15
skimmianine ( <b>22</b> ) . . . . .	<i>A. baueri</i>	lf	7

<sup>a</sup>lf=leaf, bk=bark, wd=wood.

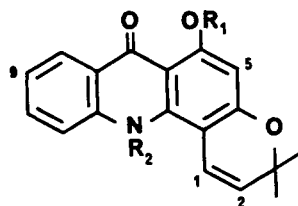
<sup>b</sup>This paper.

acrid-9-one alkaloid, and the mass spectrum with an  $M^+$  at  $m/z$  299 indicated the isolate to be an isomer of **9**. The pmr spectrum confirmed the close structural relationship with three methoxyl groups, one *N*-methyl group, a three-proton multiplet of aromatic protons, a doublet at  $\delta$  8.35 for the proton *peri* to the carbonyl, and finally a singlet aromatic proton at  $\delta$  6.39. On this basis, two structures, the 1,2,4-trimethoxy- and the 1,3,4-trimethoxy- isomers of 10-methyl acridone, were proposed. Direct comparison of the isolate with an authentic sample of 1,3,4-trimethoxy-10-methyl acridone (**10**) established the identity.

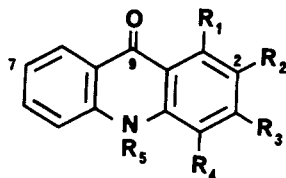
1,3,4-Trimethoxy-10-methyl acridone (**10**) has been synthesized by Hughes and co-workers (30) and subsequently synthesized and isolated from *Teclea boiviviana* (Rutaceae) by Vaquette *et al.* (26). No other previous isolations have been reported.

TABLE 2. Miscellaneous Compounds Isolated from *Acronychnia* Species

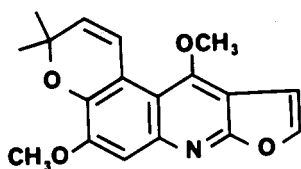
Compound	Plant	Plant part <sup>a</sup>	Reference
Acronylin . . . . .	<i>A. pedunculata</i>	bk	16
6-Demethylacronylin . . . . .	<i>A. pedunculata</i>	rt bk	17
Methyl 4-geranyloxy-cinnamate . . . . .	<i>A. baueri</i>	bk	9,13
Methyl 4-geranyloxy-3-methoxy-cinnamate . . . . .	<i>A. baueri</i>	bk	13
Geranyl coumarate methyl ether . . . . .	<i>A. baueri</i>	bk	9
Acrovestone . . . . .	<i>A. pedunculata</i>	bk	18,19
	<i>A. vestita</i> F.v. Muell.	bk	20
(+)-Asarinin . . . . .	<i>A. muelleri</i> (Engl.) Francis	lf	21
$\alpha$ -Pinene . . . . .	<i>A. pedunculata</i>	lf	22
Limonene . . . . .	<i>A. pedunculata</i>	lf	22
Baurenol . . . . .	<i>A. baueri</i>	bk	13,23
	<i>A. pedunculata</i>	st bk	24
$\beta$ -Sitosterol . . . . .	<i>A. baueri</i>	bk	9
	<i>A. pedunculata</i>	wd	22,25
Lupeol . . . . .	<i>A. baueri</i>	bk	2,9
Stigmasterol . . . . .	<i>A. baueri</i>	bk	9
K Oxalate . . . . .	<i>A. pedunculata</i>	st bk	24

<sup>a</sup>bk=bark, rt=roots, lf=leaf, st=stem.

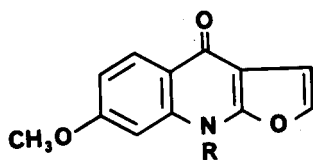
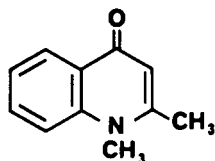
	R <sub>1</sub>	R <sub>2</sub>
<b>1</b>	CH <sub>3</sub>	CH <sub>3</sub>
<b>2</b>	H	CH <sub>3</sub>
<b>14</b>	CH <sub>3</sub>	H



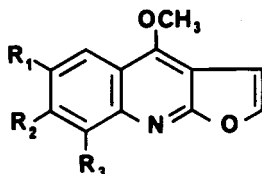
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>
<b>3</b>	OCH <sub>3</sub>	H	OCH <sub>3</sub>	H	CH <sub>3</sub>
<b>4</b>	OH	OCH <sub>3</sub>	OCH <sub>3</sub>	H	CH <sub>3</sub>
<b>5</b>	OH	OCH <sub>3</sub>	-OCH <sub>2</sub> O-		CH <sub>3</sub>
<b>6</b>	OH	-OCH <sub>2</sub> O-		OCH <sub>3</sub>	CH <sub>3</sub>
<b>7</b>	OCH <sub>3</sub>	-OCH <sub>2</sub> O-		OCH <sub>3</sub>	H
<b>8</b>	OCH <sub>3</sub>	OCH <sub>3</sub>	-OCH <sub>2</sub> O-		CH <sub>3</sub>
<b>9</b>	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	H	CH <sub>3</sub>
<b>10</b>	OCH <sub>3</sub>	H	OCH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>
<b>11</b>	OCH <sub>3</sub>	-OCH <sub>2</sub> O-		OCH <sub>3</sub>	CH <sub>3</sub>
<b>12</b>	OH	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>
<b>13</b>	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>



15

16 R = -CH<sub>2</sub>CH=C(CH<sub>3</sub>)<sub>2</sub>17 R = -CH<sub>2</sub>CH<sub>2</sub>C(OH)(CH<sub>3</sub>)<sub>2</sub>

18



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
19	H	H	H
20	H	OCH <sub>3</sub>	H
21	OCH <sub>3</sub>	OCH <sub>3</sub>	H
22	H	OCH <sub>3</sub>	OCH <sub>3</sub>

From its uv spectrum, normelicopine (**5**) was shown to be an acrid-9-one alkaloid, and it, too, displayed a molecular ion at  $m/z$  299. Two methoxyl and/or *N*-methyl signals, a methylenedioxy signal ( $\delta$  5.99), and a strongly H-bonded phenolic OH signal ( $\delta$  15.05) were observed in the pmr spectrum together with four coupled aromatic protons, including a strongly deshielded ( $\delta$  8.35) doublet of doublets. These data suggested two alternative structures, normelicopine (**5**) or normelicopidine (**6**), and direct comparison with an authentic sample of **5** (**9**) established the identity.

Normelicopine (**5**) has been isolated previously from *A. baueri* bark (**9**), and the compound has been synthesized from melicopine by demethylation (**32**).

Noracronycine revealed a uv spectrum typical of a member of the acronycine series of alkaloids (**4**) and displayed a molecular ion at  $m/z$  307, 14 mass units less than acronycine (**1**). The pmr spectrum displayed a six-proton singlet for a geminal methyl group, one *N*-methyl (or *O*-methyl) group, a pair of doublets ( $J=9.6$  Hz) for the olefinic protons, a singlet aromatic proton ( $\delta$  6.19), and four coupled aromatic protons. Most significant was a hydrogen-bonded hydroxyl proton at  $\delta$  14.68, which suggested that the isolated compound was noracronycine (**2**).<sup>2</sup> Comparison with an authentic sample, from the demethylation of acronycine (**3**), confirmed the identity.

Noracronycine (**2**) is an established natural product, having been isolated previously from *Glycosmis pentaphylla* (**33**), *Murraya paniculata* (**34**), and *Boeninghausenia albiflora* (**35**). It has also been an intermediate in the synthesis of acronycine (**1**) (**36-38**).

Des-*N*-methyl acronycine also displayed a uv spectrum typical of an acronycine-like alkaloid (**3**), and a molecular ion at  $m/z$  307, indicating it be isomeric with **2**. In the pmr spectrum, signals for a pair of doublets ( $J=10.0$  Hz) were observed at  $\delta$  5.53 and 6.81, a singlet at  $\delta$  1.47 for the geminal methyl protons, a singlet at  $\delta$  6.16 for an aromatic proton, four coupled aromatic protons and a methoxyl (or *N*-methyl) singlet at  $\delta$  3.88. Substitution on the A-ring was established by the observation of a strongly deshielded doublet at  $\delta$  8.31 for the proton *peri* to the carbonyl. No strongly hydrogen-bonded protons were observed. The accumulated data suggested that the isolated compound was des-*N*-methyl acronycine (**14**), and direct comparison with an authentic

<sup>2</sup>A more detailed discussion of the high-field proton nmr spectra of acronycine derivatives may be found in reference 6.

sample confirmed the identity. The alkaloid has previously been isolated from *G. pentaphylla* (33) and *M. paniculata* (34) and synthesized *en route* to acronycine (**1**) (39,40).

All of the isolates described above are new to the genus *Acronychia*, with the exception of normelicopine (**5**).

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined using a Kofler hot stage microscope and are uncorrected. Ir spectra were recorded with a Beckman model IR 18-A spectrophotometer with polystyrene calibration at  $1601\text{ cm}^{-1}$  or with a Nicolet MX-1 FT-IR interferometer; absorption bands are recorded in wave numbers ( $\text{cm}^{-1}$ ). Uv spectra were measured with a Beckman model DB-G spectrophotometer. Pmr spectra were recorded in  $\text{CDCl}_3$  or  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  with a Varian T-60A instrument operating at 60 MHz and having a Nicolet Model TT-7 Fourier Transform attachment. High field nuclear magnetic resonance spectra were obtained at the Midwest Regional NMR Facility, University of Illinois at Urbana, on a Nicolet NT-360 instrument. Mass spectra were taken on a Varian MAT 1125 double focusing spectrometer.

ISOLATION OF (**5**), (**9**), (**10**), (**14**), AND (**2**).—A crude, acronycine-containing mixture of alkaloids from the bark of *Acronychia baueri* (100 g) was chromatographed over a column of neutral alumina<sup>3</sup> eluting with  $\text{C}_6\text{H}_6\text{-CHCl}_3$  and subsequently silica gel<sup>4</sup> eluting with  $\text{CHCl}_3\text{-MeOH}$ . Repeated chromatography of the most polar fraction (4.905 g) on silica gel followed by preparative tlc on silica gel 60<sup>4</sup> afforded 1,2,3-trimethoxy-10-methylacridone (**9**), 1,3,4-trimethoxy-10-methylacridone (**10**), and des-*N*-methylacronycine (**14**). Chromatography of the acronycine-containing mixture on silica gel without passage through alumina afforded, after preparative tlc, normelicopine (**5**) and noracronycine (**2**).

Normelicopine (**5**, 3.1 mg) was obtained as red needles from  $\text{CHCl}_3$ , mp  $234\text{-}236^\circ$  [Lit.  $235.5\text{-}236.5^\circ$  (32)]; ir  $\nu$  max (KBr) 1575, 1446, 1361, 1321, 1266, 1166, 1127, and  $1066\text{ cm}^{-1}$ ; uv  $\lambda$  max (EtOH) 251 (log  $\epsilon$  3.27), 279 (3.32), 315 (3.11), and 431 nm (2.62); pmr (60 MHz,  $\text{CDCl}_3$ )  $\delta$  3.96 (s, 3H,  $-\text{OCH}_3$ ), 4.00 (s, 3H,  $-\text{NCH}_3$ ), 5.99 (s, 2H,  $-\text{OCH}_2\text{O}-$ ), 7.07-7.81 (m, 3H, C5-H, C6-H and C7-H), 8.35 (dd, 1H,  $J=1.6, 7.9$  Hz), and 15.05 (s, 1H,  $-\text{OH}$ ); ms  $m/z$  (rel. int.) 300 (16), 299 ( $\text{M}^+$ , 86), 285 (17), 284 (100), 254 (34), 170 (10), 158 (26), and 115 (17). Identification was established through comparison with an authentic, synthetic sample.

1,2,3-Trimethoxy-10-methylacridone (**9**, 11.7 mg) was obtained as pale yellow, rhomboid crystals from  $\text{CHCl}_3\text{-MeOH}$ , mp  $157\text{-}160^\circ$  [Lit.  $116\text{-}118^\circ$  (30)]; ir  $\nu$  max (KBr) 1623, 1603, 1496, 1477, 1257, 1192, 1139, 1125, 1100, and  $1051\text{ cm}^{-1}$ ; uv  $\lambda$  max (EtOH) 272 (log  $\epsilon$  3.29) and 393 nm (2.60); pmr (360 MHz,  $\text{CDCl}_3$ )  $\delta$  3.851 (s, 3H,  $-\text{NCH}_3$ ), 3.927 (s, 3H, C1- $\text{OCH}_3$  or C2- $\text{OCH}_3$ ), 4.035 (s, 3H, C3- $\text{OCH}_3$ ), 4.046 (s, 3H, C2- $\text{OCH}_3$  or C1- $\text{OCH}_3$ ), 6.627 (s, 1H, C4-H), 7.270 (ddd, 1H,  $J=0.7, 7.0, 8.0$  Hz, C7-H), 7.448 (dd, 1H,  $J=0.7, 8.6$  Hz, C5-H), 7.665 (ddd, 1H,  $J=1.6, 7.0, 8.6$  Hz, C6-H), and 8.513 (dd, 1H,  $J=1.6, 8.0$  Hz, C8-H); ms  $m/z$  (rel. int.) 300 (7), 299 ( $\text{M}^+$ , 39), 285 (17), 284 (100), 266 (5), 256 (10), 254 (6), 241 (11), 226 (6), 142.5 (6), 142 (38), 141.5 (7), 127 (9), and 119.5 (13).

1,3,4-Trimethoxy-10-methyl acridone (**10**, 9.3 mg) was obtained as pale yellow, rhomboid crystals from EtOAc, mp  $134\text{-}137^\circ$  [Lit.  $137^\circ$  (26)]; ir  $\nu$  max 1638, 1601, 1589, 1462, 1321, 1210, 1203, 1173, 1096, and  $1052\text{ cm}^{-1}$ ; uv  $\lambda$  max (EtOH) 264 (log  $\epsilon$  4.01), 295 (3.46), and 394 nm (3.26); pmr (60 MHz,  $\text{CDCl}_3$ )  $\delta$  3.70 (s, 3H,  $-\text{NCH}_3$ ), 3.90 (s, 3H,  $-\text{OCH}_3$ ), 3.99 (s, 6H, 2 x  $-\text{OCH}_3$ ), 6.39 (s, 1H, C2-H), 7.04-7.76 (m, 3H, C5-H, C6-H and C7-H), and 8.35 (dd, 1H,  $J=1.4, 7.8$  Hz, C8-H); ms  $m/z$  (rel. int.) 300 (17), 299 ( $\text{M}^+$ , 91), 284 (100), 270 (8), 255 (9), 254 (12), 241 (12), 240 (59), 266 (11), 255 (8), 212 (9), 184 (6), 183 (5), 170 (8), 149.5 (14), 128 (7), 127 (9), and 105 (8). Identification was confirmed by direct comparison with an authentic sample.<sup>2</sup>

Des-*N*-methylacronycine (**14**, 14.6 mg) was obtained as pale yellow, fine prisms from  $\text{CHCl}_3\text{-MeOH}$ , mp  $253\text{-}256^\circ$  [Lit.  $268\text{-}270^\circ$  (33),  $218\text{-}219^\circ$  (39),  $237\text{-}240^\circ$  (40)]; ir  $\nu$  max (KBr) 3530, 3325, 3200, 3130, 2975, 1630, 1600, 1575, 1535, 1355, 1313, 1202, 1143, 1104, and  $756\text{ cm}^{-1}$ ; uv  $\lambda$  max (EtOH) 252 (sh) (log  $\epsilon$  3.60), 266 (3.76), 283 (3.55), 293 (3.58), 307 (3.18), 335 (2.73), and 391 nm (2.96);  $\lambda$  max (EtOH+KOH) 252 (sh), 266, 275 (sh), 293, 307, 335, 398, 425 (sh), and 451 nm; pmr (60 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$ )  $\delta$  1.47 (s, 6H,  $-\text{C}(\text{CH}_3)_2$ ), 3.88 (s, 3H,  $-\text{OCH}_3$ ), 5.53 (d, 1H,  $J=10.0$  Hz, C2-H), 6.16 (s, 1H, C5-H), 6.81 (d, 1H,  $J=10.0$  Hz, C1-H), 6.97-7.50 (m, 3H, C9-H, C10-H and C11-H), and 8.31 (bd d, 1H,  $J=8.0$  Hz, C8-H); ms  $m/z$  (rel. int.) 308 (31), 307 ( $\text{M}^+$ , 100), 293 (50), 292 (100), 278 (38), 277 (21), 264 (13), 263 (45), 262 (35), 249 (14), 248 (19), 220 (12), 153.5 (16), 146 (33), 145.5 (11), 131.5 (19), 131 (27), 117 (19), and 102 (17). Identification was confirmed by direct comparison with an authentic sample.<sup>4</sup>

Noracronycine (**2**, 6.5 mg) was obtained from  $\text{CHCl}_3$  as yellow needles, mp  $200.5\text{-}201^\circ$ ; ir  $\nu$  max

<sup>3</sup>Fisher Scientific Co., Fairlawn, NJ.

<sup>4</sup>E. Merck, Darmstadt, West Germany.

(KBr) 1633, 1590, 1569, 1549, 1478, 1333, 1273, 1172, 1146, and 755  $\text{cm}^{-1}$ ; uv  $\lambda$  max (EtOH) 227 (log  $\epsilon$  4.22), 256 (4.41), 284 (4.68), 295 (sh, 4.63), 312 (4.37), 342 (sh, 3.68), and 410 nm (3.69); pmr (60 MHz,  $\text{CDCl}_3$ )  $\delta$  1.50 (s, 6H,  $-\text{C}(\text{CH}_3)_2$ ), 3.83 (s, 3H,  $-\text{NCH}_3$ ), 5.45 (d, 1H,  $J=9.6$  Hz, C2-H), 6.19 (s, 1H, C5-H), 6.50 (d, 1H,  $J=9.6$  Hz, C1-H), 7.08-7.75 (m, 3H, C9-H and C11-H), 8.26 (d, 1H,  $J=7.6$  Hz, C8-H) and 14.68 (s, 1H, -OH); ms  $m/z$  (rel. int.) 308 (7), 307 ( $\text{M}^+$ , 32), 293 (21), 292 (100), 278 (8), 277 (34), 146 (12), 132 (6), and 124.5 (9).

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