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DITERPENE AND ANTHRAQUINONE CONSTITUENTS OF *GLYCYDENDRON AMAZONICUM*

WINSTON F. TINTO, GREGORY BLYDEN,

Centre for Natural Products Chemistry, University of Guyana, Georgetown, Guyana

WILLIAM F. REYNOLDS, and STEWART McLEAN*

Department of Chemistry, University of Toronto, Toronto, Canada, M5S 1A1

ABSTRACT.—The diterpenes abbeokutone [1] and 1,2-dehydroabbeokutone [2] have been isolated from *Glycydendron amazonicum*. Two-dimensional nmr spectroscopy has been used to make structural and spectroscopic assignments. A small amount of 1,6-dimethyl-2,7-dimethoxyanthraquinone [3], a new compound, was also isolated.

Roots and bark of *Glycydendron amazonicum* Ducke (Euphorbiaceae), a canopy tree of the forest in the near interior of Guyana that appears not to have received previous phytochemical attention, have been examined. The root extract afforded the diterpene abbeokutone [1] (1,2). When it was first isolated, this compound was investigated by routine spectroscopic methods, including 2D-nmr spectroscopy. After one-bond ^{13}C-^{1}H connectivities had been established (HETCOR experiment), our XCORFE pulse sequence (3) was used to identify two- and three-bond connectivities. The results, summarized in Table 1, showed that the compound was a 3-oxo-16,17-dihydroxykaurane; its physical properties, and those of its monoacetate, were in accord with those reported for the stereoisomer abbeokutone [1] (1,2). Confirmation was obtained by periodate cleavage that converted the diol to a diketone with physical properties in agreement with those reported for 17-nor-(−)-kaurane-3,16-dione (4). It became

apparent that the extract contained an α,β-unsaturated ketone that was initially difficult to separate from 1. This compound was isolated (without abbeokutone) from the bark extract. Its spectroscopic characteristics show that it is 1,2-dehydroabbeokutone [2]. Of particular importance was the appearance in the ^{1}H-nmr spectrum of one-proton doublets ($J = 10.1$ Hz) at δ 7.14 and 5.82; the ^{13}C-nmr spectrum (Table 2) is in accord with a structure that differs from abbeokutone only in ring A. This previously undescribed compound has very recently been reported as a constituent of *Mallotus anomalus* (Euphorbiaceae) from China, and the name anomaluone has been assigned to it (5).

The bark extract also provided a very small amount of an anthraquinone **3**. The nmr evidence clearly shows the presence of two methyl and two methoxyl substituents on a 1,2,6,7-substituted anthraquinone; evidence from a ^{1}H-^{1}H nOe experiment shows that the δ 2.20 methyl group is adjacent to an aromatic proton (δ 7.83 singlet) and the δ 4.00 methoxyl group is next to the other iso-
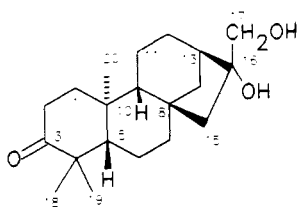
1
2 (1,2-dehydro)
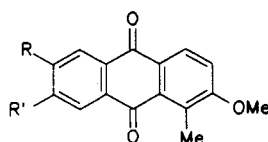
3 R=Me, R'=MeO
4 R=MeO, R'=Me

TABLE 1. Assigned Chemical Shifts and Connectivities for
Abbeokutone [1].[a]

Carbon	δ_C	δ_H	2- and 3-bond connectivities
C-1	39.16	1.34, 1.95	2.44, 1.06
C-2	33.94	<2.44>[b]	1.95, 1.34
C-3	218.18	—	2.44, 1.06, 1.01
C-4	47.11	—	1.06, 1.01
C-5	54.20	1.38	1.06
C-6	21.59	1.42, 1.49	1.38
C-7	40.82	1.47, 1.63	1.49
C-8	44.34	—	2.04
C-9	55.28	1.08	1.47, 1.06
C-10	38.40	—	1.06
C-11	18.75	<1.57>[b]	
C-12	25.97	1.50, 1.60	1.57
C-13	45.15	2.04	3.67, 1.61
C-14	36.79	1.61, 1.87	1.52
C-15	52.62	1.39, 1.52	1.87
C-16	81.69	—	1.87
C-17	66.14	3.67, 3.77	1.52
C-18	27.19	1.06	1.01
C-19	20.87	1.01	1.06
C-20	17.72	1.06	1.08

[a]Data are for solutions in $CDCl_3$. Chemical shifts were measured at
100.6 MHz for ^{13}C and 400 MHz for ^1H. Assignments of δ_H values are
based on a 1-bond connectivity experiment (HETCOR). Column 4
lists δ_H values for observed cross peaks to ^{13}C in an XCORFE experi-
ment.
[b]Mean values for incompletely resolved CH_2 multiplets.

lated proton (δ 7.15 singlet), while the δ
3.89 methoxyl group is adjacent to the δ
7.07 proton that has a coupling of 8.7
Hz to its ortho neighbor (δ 7.73). Only
two structures, 1,6-dimethyl-2,7-di-
methoxyanthraquinone [3] and 1,7-di-
methyl-2,6-dimethoxyanthraquinone
[4], are compatible with these data, and
neither has been described previously.
Unfortunately, the decomposition of the
sample prevented an unambiguous dis-
tinction on the basis of selective INEPT
or experiments using heteronuclear nOe
or decoupling. However, the relatively
large chemical shift difference between
the two carbonyl carbons (δ 185.2, δ
180.9) clearly favors 3. Substituent-in-
duced chemical shifts in 2-methoxyan-
thraquinone (6) and 1-methyl- and 2-
methylanthraquinone (7–9) have been
used to predict C-9 and C-10 chemical
shifts in 3 and 4 (Table 3). The observed

values for both the C-9 chemical shift
and the chemical shift difference be-
tween C-9 and C-10 are much closer to
those predicted for 3 than to those for 4.
Consequently, the quinone is assigned
structure 3.

EXPERIMENTAL

PLANT MATERIAL.—Plants were collected in
the Essequibo region of Guyana. Voucher speci-
mens are deposited at the Herbarium of the Uni-

TABLE 2. ^{13}C Chemical Shifts of Abbeokutone [1] and Derivatives.[a]

Carbon	Compound			
	1	**1-Ac**	nordione	**2**
C-1 . . .	39.2	38.9	39.1	160.1
C-2 . . .	33.9	33.7	33.9	125.6
C-3 . . .	218.2	217.7	217.5	205.5
C-4 . . .	47.1	46.9	47.1	43.7
C-5 . . .	54.2	54.0	54.2	53.3
C-6 . . .	21.6	21.4	20.3	20.4
C-7 . . .	40.8	40.5	39.9	41.0
C-8 . . .	44.3	44.3	42.2	44.7
C-9 . . .	55.3	55.0	53.6	50.2
C-10 . . .	38.4	38.2	38.5	41.3
C-11 . . .	18.8	18.5	19.0	19.0
C-12 . . .	26.0	25.8	29.3	26.5
C-13 . . .	45.2	45.6	47.6	40.5
C-14 . . .	36.8	36.5	37.0	38.6
C-15 . . .	52.6	52.4	54.6	52.1
C-16 . . .	81.7	79.5	221.8	79.6
C-17 . . .	66.1	68.2	—	69.8
C-18 . . .	27.2	27.1	27.3	28.3
C-19 . . .	20.9	20.8	21.0	21.1
C-20 . . .	17.7	17.6	18.1	21.3
Me*CO* . .	—	171.1	—	—
*Me*CO . .	—	20.7	—	—

[a]Chemical shifts for **1** (Table 1) provide benchmark; chemical shifts for derivatives assigned empirically.

versity of Guyana, and at the Institute of Systematic Botany, University of Utrecht, Netherlands.

EXTRACTION.—Dried, ground roots (1 kg) were extracted with 95% EtOH to provide a solid (16.3 g). Flash chromatography of a portion (5 g) with elution by CHCl$_3$ yielded **1** (1.73 g).

Dried, ground bark (845 g) was extracted with CH$_2$Cl$_2$-MeOH (3:5) to provide material (14 g)

TABLE 3.   Predicted Chemical Shifts for C-9 and C-10 in **3** and **4** and Observed C-9 and C-10 Chemical Shifts.

	δ_{C-9}	δ_{C-10}	$\delta_{C-9}-\delta_{C-10}$
Predicted for **3**[a]	184.2	180.1	4.1
Predicted for **4**[a]	182.9	181.4	1.5
Observed	185.2	180.9	4.3

[a]Using substituent-induced chemical shifts for a 2-MeO group (6) and average substituent-induced chemical shifts for 1-Me (7,8) and for 2-Me groups (8,9) in anthraquinone derivatives. Substituent effects are assumed to be additive.

that was dissolved in MeOH-H$_2$O (9:1) and extracted with hexane. The MeOH/H$_2$O solution was diluted with H$_2$O until 40% aqueous and extracted with Et$_2$O. This extract yielded a solid (4 g) that was chromatographed on SiO$_2$ with elution by Me$_2$CO/hexane mixtures. A 1:10 solvent mixture eluted **3** (5 mg), and a 1:6 mixture eluted **2** (32 mg).

Abbeokutone [1].—Mp 189–193°; [α]D −80° (c = 0.4, CHCl$_3$); ir (KBr) 3400 (broad), 1707; ms 320 (4), 302 (6), 289 (100), 271 (38), 247 (18), 229 (16), 145 (21), 107 (24); exact mass 320.2351, calcd for C$_{20}$H$_{32}$O$_3$, 320.2351. Cold Ac$_2$O/pyridine treatment gave a monoacetate, mp 130–132°, [α]D −75° (c = 0.35, CHCl$_3$). Treatment of **1** (27 mg) in MeOH with NaIO$_4$ provided 17-nor-(−)-kaurane-3,16-dione (16 mg): mp 148–150°, ir(KBr) 1738, 1703; ms 288 (100), 273 (12), 245 (25), 233 (40), 203 (68), 190 (43), 177 (27), 159 (29); exact mass 288.2104, calcd for C$_{19}$H$_{28}$O$_2$, 288.2089.

1,2-Dehydroabbeokutone [2].—Mp 203–205°; [α]D −71° (c = 0.16, CHCl$_3$); ir (CHCl$_3$) 3440 (broad), 1664, uv 225 (5900); ms 318 (17), 300 (21), 287 (100), 203 (18), 185 (19), 163 (75), 137 (91); exact mass 318.2195, calcd for C$_{20}$H$_{30}$O$_3$, 318.2195.

1,6-Dimethyl-2,7-dimethoxy-9,10-anthraquinone [3].—Mp 275–278°; ir (KBr) 1665, 1659, 1608; uv 222 (14,000), 281 (8,300), 298 (3,800), 375 (2300); ^{1}H nmr (400 MHz) 7.83 (s, 1H), 7.72 (d, 8.7 Hz, 1H), 7.15 (s, 1H), 7.07 (d, 8.7, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 2.54 (s, 3H), 2.20 (s, 3H); ^{13}C nmr (100 MHz) 185.2 (e), 180.9 (e), 164.3 (e), 158.8 (e), 137.9 (e), 133.8 (e), 132.0 (o), 130.6 (e), 129.0 (e), 128.0 (e), 123.1 (e), 122.7 (o), 115.5 (o), 103.9 (o), 56.0 (o), 55.7 (o), 15.7 (o), 13.4 (o); ms *m/z* 296 (100), 268 (69), 243 (51), 225 (34).

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