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THREE GUAIANOLIDES FROM *BAHIA OPPOSITIFOLIA*

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Key Word Index—*Bahia oppositifolia*; Compositae; sesquiterpene lactones; des-sarracinyl bahia-III; 1,10-hydrobahia-III; bahia-III.

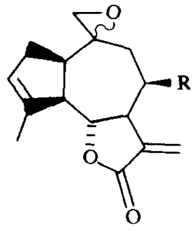
Abstract—Three new guaianolides have been isolated from *Bahia oppositifolia* along with the previously reported bahifolin. Compounds were isolated and purified by extraction and chromatographic techniques, while identification was carried out by spectral means. The ^{13}C NMR data for bahifolin and des-sarracinyl bahia-III are given.

INTRODUCTION

Several sesquiterpene lactones have been isolated from *Bahia* species including woodhousin (**1**) from *B. woodhousin* [1], bahia-I (**2**) and bahia-II (**3**) from both *B. absinthifolia* and *B. pringlei* [2]. *B. oppositifolia* has already been shown [3] to contain bahifolin (**4**). This paper reports the isolation of three new guaianolides, des-sarracinyl bahia-III (**5**), 1,10-hydrobahia-III (**6**) and bahia-III (**7**) from *B. oppositifolia.*

RESULTS AND DISCUSSION

All four of the compounds isolated from *Bahia oppositifolia* (Nutt.) were guaianolides. The three new compounds are referred to as des-sarracinyl bahia-III, 1,10-hydrobahia-III and bahia-III, following the format established by Romo de Vera and Ortega [2]. The occurrence of the exocyclic double bond on the lactone ring was supported by IR bands at 1760 and 1615 cm^{-1} (C=C) and by strong UV absorbtion around 210 nm, $\varepsilon = 10000$/M cm [4] and the characteristic ^{1}H NMR doublet of doublets around δ 6.0. ^{1}H NMR spectra showed coupling constants between H-6 and H-8 ($J = 8.4$ Hz) and splitting patterns consistent with a *trans* C-6 closure. The complexity of the H-7 signal was greatly increased by coupling from the two H-13*s* ($J = 3.1$, 3.5 Hz) and H-8 ($J = 4.0$ Hz) which required spin decoupling experiments for full evaluation. Trisubstituted double bond systems were supported by IR peaks at 3030 and 785 cm^{-1} ($\text{H-}\underset{|}{\text{C}}=\text{C}<$) and 1630 (C=C). Elemental analyses were consistent with the proposed structures, after the presence of small amounts of silica gel were accounted for.



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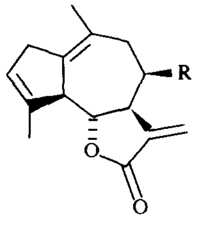

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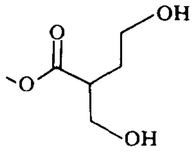

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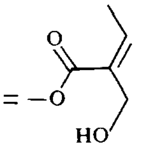

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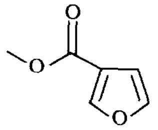

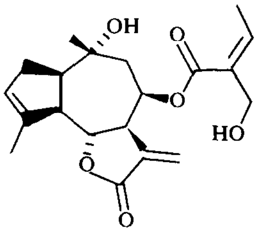

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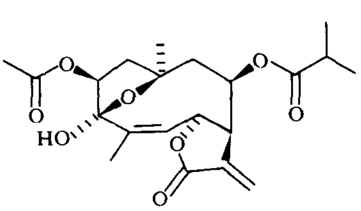

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One of the compounds isolated was identified as bahifolin (**4**). The identification of this compound was based mainly on the similarities between it and values reported by Hertz *et al.* [3]. Enough material was available to run a ^{13}C NMR on the bahifolin, and the results (Table 1) agreed with the published structure.

A second compound isolated from *B. oppositifolia* was dessarracinyl bahia-III (**5**). The mass spectrum was EIMS (probe) 70 eV, *m/z* (rel. int.): 246 $[M]^+$. An alcoholic function was supported by IR bands at 3400 and 1120 ($>C-OH$). The coupling constant between the H-7 and H-8 ($J = 4.0$ Hz) indicates an axial–equatorial orientation, which is consistent with a β-hydroxyl group. The orientation of this group was checked by the method developed by Horeau [5]. The recovered acid was dextrorotatory, i.e. an *R* configuration around C-8.

The ^{13}C NMR for des-sarracinyl bahia-III is given in Table 1. Assignment of peaks is based partially on the results of calculations based on the additivity rules [6].

1,10-Hydrobahia-III (**6**) was basically similar to the other compounds isolated from this species. The mass spectrum was EIMS (probe) 70 eV, *m/z* (rel. int.): 362 $[M]^+$ (15), 345 $[M-OH]^+$ (9), 246 $[M-H-C_5H_7O_3]^+$ (12), 229 $[M-H_2O-C_5H_7O_3]^+$ (100), 99 $[C_5H_7O_2]^+$ (39). The sarracinate ester side chain would be the most common fitting this pattern. The weight of the base ion suggested the guaianolide skeleton, plus an additional oxygen. This oxygen was most likely an alcohol since IR peaks at 3400 and 1145 ($>C-OH$) were observed. Also seen were peaks at 1730 (C=O) 1665 (C=C, 2′/3′) and 1630 (C=C, 3/4). The ^1H NMR data given for C-6 and C-8 both indicate bonding to an oxygen atom, suggesting one is the site of the ester side chain and the other is the closure of the lactone ring. The upfield value is more characteristic of the ring closure, and the splitting pattern is consistent with the environment of C-6. Coupling was seen between H-3′ and H-4′ ($J = 6.5$ Hz) and with H-5′ ($J = 1.8$ Hz) via the double bond. It should be mentioned that the *Z*-isomer of the sarracinate side chain would fit the data just as well as the suggested structure, but this particular side chain has not been reported, while the sarracinate side chain is fairly common.

Bahia-III (**7**) proved to be an esterified guaianolide. The mass spectrum gave EIMS (probe) 70 eV, *m/z* (rel. int.): 344 $[M]^+$ (9), 288 $[M-H-C_5H_7O_3]^+$ (100), 99 $[C_5H_7O_2]^+$ (41), again suggesting a sarracinate ester side chain.

Most of the spectral characteristics seen for 1,10-hydrobahia-III were also seen for bahia-III. The IR showed peaks at 1630 (C=C, 3/4) and 1664 (C=C, 2′/3′), plus bands at 3030 and 780 cm^{-1} ($H-\underset{|}{C}=C<$). Bands were also seen at 3405, 1045 ($>C-OH$) and 1725 cm^{-1} (C=O). From the ^1H NMR data in Table 1, the ester side chain can be seen, with H-3′ coupled with H-4′ ($J = 6.6$ Hz).

As would be expected from the structures of des-sarracinyl bahia-III, 1,10-hydrobahia-III and bahia-III, the compounds are closely related, and 1,10-hydrobahia-III may simply be the hydrated product of bahia-III, which in turn may be an esterified product of des-sarracinyl bahia-III. Because of these close similarities, it seems reasonable to postulate that the stereochemistry of these three compounds are similar.

EXPERIMENTAL

Specimens of *Bahia oppositifolia* (Nutt.), voucher No. RM 290612, were collected along public roads in southern Albany

Table 1. ^1H and ^{13}C NMR spectral data for *B. oppositifolia* sesquiterpene lactones (d_6-Me_2CO, TMS internal standard, 269.65 MHz)

	5	**6**	**7**		**4**	**5**
H-1	—	2.35(1)*m**	—	C-1	51	142
H-2	2.78(2)*d*	2.75(2)*dd*	2.73(2)*d*	C-2	37	35
H-3	5.57(1)*m*	5.49(1)*m*	—	C-3	122	121
H-5	2.30(1)*m**	2.35(1)*m**	2.30(1)*m**	C-4	147	147
H-6	4.11(1)*dd*	3.51(1)*m*	3.52(1)*m*	C-5	34	33
H-7	3.56(1)*m*	3.51(1)*m*	3.52(1)*m*	C-6	50	52
H-8	3.91(1)*m*	3.78(1)*m*	4.07(1)*m*	C-7	68	67
H-9	2.30(2)*m**	2.35(3)*m**	2.30(2)*m**	C-8	57	59
H-13a	6.17(1)*d*	6.26(1)*d*	1.16(1)*d*	C-9	81	80
H-13b	5.77(1)*d*	5.80(1)*d*	5.83(1)*d*	C-10	60	132
H-14	2.30(3)*m**	1.23(3)*s*	2.30(3)*m**	C-11	180	169
H-15	1.89(3)*d*	1.93(3)*d*	1.92(3)*d*	C-12	207†	210†
				C-13	132	136
H-3′	—	6.35(1)*dd*	6.44(1)*dd*	C-14	54	15
H-4′	—	2.05(3)*dd*	1.98(3)*dd*	C-15	17	18
H-5′	—	4.16(2)*dd*	4.13(3)*dd*	C-1′	205†	—
				C-2′	177	—
				C-3′	127	—
				C-4′	146	—
				C-5′	153	—

J (Hz): 3,15 = 1.5; 5,6 = 9.5; 6,7 = 8.5; 7,8 = 4.0; 7,13a = 3.1; 7,13b = 3.5; compound **5**, 8,9 = 9.9; compound **6** 3′,4′ = 7.5; compound **7**, 3′,4′ = 7.2.

*Part of a complex multiplet between δ 2.20 and 2.50.

†Observed as shoulders on the carbonyl of the solvent peak.

County, Wyoming, during July 1981. A total of five $CHCl_3$ extractions were carried out on the above-ground portions which resulted in a dark viscous soln.

The crude soln was washed ×3 with equal vols. of 50% EtOH–H_2O. Further purification was carried out on a silica gel column, eluted with a $CHCl_3$–C_6H_6 (1:1, 3:1); $CHCl_3$; Me_2CO–$CHCl_3$ (1:3, 1:1, 3:1); Me_2CO series. Fractions containing sesquiterpene lactones were pooled and the solvent evapd off yielding a clear to yellowish amorphous residue.

Routine analysis of fractions was carried out on precoated silica gel 60 F-254 plates. Plates were developed in 50% Me_2CO–CH_2Cl_2 and visualized with H_2SO_4. Fractions were then chromatographed on preparative 2 mm silica gel 60 F-254 plates, 20 × 20 cm. A small amount of extract was spotted 0.5 cm in from each side of the plate, with the bulk of the material being spotted in a band lying 1.5 cm in from each edge. The plates were developed and a piece of Al foil was used to protect the main band while the outside spots were sprayed with H_2SO_4. The band between the two spots was then removed from the plate, and the sesquiterpene lactones displaced into an Me_2CO soln. The silica gel was removed by careful filtration and centrifugation.

Crystallization was carried out by a variety of methods. Des-sarracinyl bahia-III was dissolved in Me_2CO to which a 10–15% vol. of H_2O was added. The Me_2CO was allowed to evaporate slowly allowing crystals to form in the aq. soln. The bahifolin was crystallized out of 50% MeOAc–C_6H_6. The 1,10-hydrobahia-III and bahia-III were crystallized from MeCOEt.

Samples were judged to be pure if they had a sharp mp, could be crystallized and gave a single spot on several TLC systems, including both silica gel 60 and Al_2O_3 (type T) plates developed in several solvent systems.

Identification of the different compounds isolated was based on spectral data. The NMR spectra were taken on a JEOL FX-270, ^{13}C NMR spectra were run using double accumulation, with a 2.5 μsec pulse (30°), a 2.5 sec pulse delay, 15 kHz frequency width (215 ppm) and complete decoupling. Data accumulation was carried out for 10 hr, resulting in 8500–9000 pulses. Samples were dissolved in d_6-Me_2CO. CH analysis was carried out commercially by Atlantic Microlabs Inc. of Atlanta, Georgia on des-sarracinyl bahia-III and bahifolin only, due to limitations of sample size.

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