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(−)-EPINGAIONE FROM *BONTIA DAPHNOIDES*

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Key Word Index—*Bontia daphnoides*; Myoporaceae; sesquiterpene furan; (−)-epingaione.

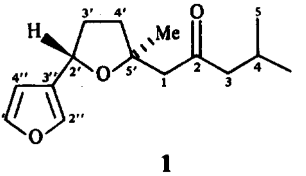
Abstract—(−)-Epingaione has been isolated as the major lipophilic metabolite of *Bontia daphnoides*, the only member of the Myoporaceae found in the West Indies.

INTRODUCTION

The Myoporaceae is a small family restricted largely to Australia except for species of *Myoporum*, extending north to China and Japan and to the islands of the Indian and Pacific Oceans, and *Bontia*, a monotypic genus, restricted to the West Indies. *Bontia* appears to be closely related to the Australian genera, differing mainly in the structure of the corolla and minor features of the fruit. Vegetatively, it is indistinguishable from species of *Myoporum*. Biochemical compatability has been established between *Myoporum* and *Bontia* as the latter has been successfully grafted onto *M. insularia* R. Br. Like other genera of the family, *Bontia* is salt-tolerant and is widely used in the Carribean as a windbreak. We have had the opportunity of examining a sample of *Bontia daphnoides* L. and now report on the isolation and identification of the sesquiterpene furan (−)-epingaione from this plant.

RESULTS AND DISCUSSION

Extraction of the leaves of a sample of *B. daphnoides* with methanol gave a dark-green extract, most of which redissolved in hot ethyl acetate. The water-soluble portion of the remaining extract crystallized from methanol and was identified as D-mannitol. ^{1}H NMR and TLC analysis of the ethyl acetate-soluble portion showed the presence of one major component, which was isolated by alumina chromatography. The compound thus obtained was essentially homogeneous, GC analysis indicating that 98% eluted as a single peak, and was shown to be (−)-epingaione (**1**) on the following evidence. Interpretation of the ^{1}H NMR and ^{13}C NMR spectra of **1** (see Table 1 and Experimental) allowed the compound to be formulated as a furanoid sesquiterpene with the constitution shown in **1**. Two diastereoisomers with this constitution are known to occur naturally in Myoporaceae. (−)-Epingaione (**1**) has the 2′*S*,5′*S*-configuration and (−)-ngaione (**2**) the 2′*S*,5′*R*-configuration [1]. A distinction between the two is not easily made on spectroscopic grounds and even the optical rotation in solution can be disturbingly similar, e.g. in benzene, (−)-ngaione has $[\alpha]_D$ −13.0° [2] compared with −14.8° for (−)-epingaione [3]. The crystalline 2,4-dinitrophenyl semicarbazone from (−)-epingaione has mp 166°, $[\alpha]_D^{CHCl_3}$ −68° and that from (−)-ngaione, mp 133–133.5°, $[\alpha]_D^{CHCl_3}$ −58° [3]. The same derivative formed from the sesquiterpene ketone from *B. daphnoides* showed mp 165–165.5° and $[\alpha]_D^{CHCl_3}$ −70° and thus the ketone must be assigned the



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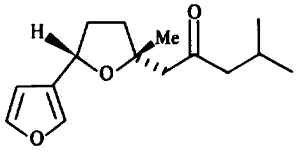

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structure of (−)-epingaione (1) [(2′S,5′S)-4-methyl-1-(5′-methyl-2′,3′,4′,5′-tetrahydro[2′,3″-bifuran]-5-yl)pentan-2-one]. A distinction between the diastereoisomers (1 and 2) can now be made on the basis of their ^{13}C NMR spectra (Table 1) which show, not unexpectedly, different chemical shifts for the 2′-, 1- and 5-methyl carbons.

(−)-Epingaione (1) and (−)-ngaione (2) have been isolated previously from *Myoporum* species and *Eremophila latrobei* [1], members of the Myoporaceae. Different races of *M. deserti** contain these compounds in varying amounts, ranging from 4.4% (dry leaf weight) of (−)-ngaione to *ca* 2.0% of (−)-epingaione [2, 3]. The sample of *Bontia* investigated contains *ca* 3.0% of (−)-epingaione together with D-mannitol, a common alditol found in members of the Myoporaceae. Interestingly, (−)-ngaione is a toxic constituent of the stock-poisoning shrub *M. deserti*, and although (−)-epingaione causes liver lesions identical with those produced by (−)-ngaione, it is not yet known whether it is toxic to sheep or cattle [3].

EXPERIMENTAL

General experimental details have been described elsewhere [6].

Extraction of Bontia daphnoides. The plant was cultivated (R.J.C.) from seeds (collection No. B895) obtained in 1978 by Mr. Kalloo in Armia, Trinidad. Leaves (50 g) collected in 1985 from a flowering plant were soaked in MeOH over 2 days. The extract obtained was taken up in hot EtOAc to give a dark-green mobile oil (1.9 g) which from TLC and ^{1}H NMR appeared to be mainly one compound with fatty material as the major contaminant. The oil was adsorbed on a column of alumina (neutral, act. III, 50 g). Elution with petrol afforded fractions containing small quantities of fats and carotenes. Further elution with diisopropyl ether gave the major component (1.0 g) as a pale yellow oil which was filtered through charcoal with Et_2O to give (−)-epingaione (1) as a colourless oil, 98% one component by GC [H 50 m ULTRA (OV1) column, H_2 as carrier gas, 50–250° at 7.5°/min]: R_t 17.75 with 2% impurity at R_t 16.76; $[\alpha]_D - 18.5°$ (*c* 6.1; $CHCl_3$), $[\alpha]_{578} - 18.8°$, $[\alpha]_{546} - 21°$, $[\alpha]_{436} - 37°$, $[\alpha]_{365} - 50°$; $[\alpha]_D - 13.4°$ (*c* 6.2; C_6H_6); $[\alpha]_D - 5.0°$ (*c* 4.6; EtOH); lit. [3] $[\alpha]_D - 14.8°$ (10% in C_6H_6); −7.3° (10% in EtOH). ^{1}H NMR (80 MHz, $CDCl_3$): δ0.92 (6H, *d*, *J* = 6.9 Hz, Me-5, 4-Me), 1.34 (3H, *br s*, 5′-Me), 2.70 (2H, *app. s*, H_2-1), 4.87 (1H, *m*, H-2′), 6.37 (1H, *m*, H-4″), 7.37 (2H, *m*, H-2″ and H-5″); ^{1}H NMR (300 MHz, CCl_4): δ0.91 (6H, *d*, *J* = 6.4 Hz, Me-5, 4-Me), 1.27 (3H, *s*, 5′-Me), 1.87 (2H, *m*) and 2.1 (2H, *m*), (H_2-3′ and H_2-4′), 2.15 (1H, *m*, H-4), 2.31 (2H, AB part of ABX, H_2-3), 2.59 (*s*, H_2-1), 4.80 (1H, *m*, X part of ABX, H-2′), 6.25 (1H, *m*, H-4″), 7.27 (1H, *m*, H-2″), 7.30 (1H, *m*, H-5″). ^{13}C NMR: see Table 1. GC/MS (OV-101, 0.31 mm × 25 m WCOT capillary, 100–240° at 20°/min) (35 eV): R_t 4.6 min, *m/z* (rel. int.): 250 $[M]^+$ (3), 150 (31), 110 (100), 95 (12), 85 (44), 83 (17), 57 (65), 43 (56).

Table 1. ^{13}C NMR spectral data of (−)-epingaione (1) and (+)-ngaione (*ent*-2)*

C	1	2		1	2
1	53.7	54.2†	4′	37.3‡	37.2‡
2	209.4	209.0	5′	81.8	81.7
3	53.7	53.6†	5′-Me	27.9	26.7
4	24.4	24.4	2″	143.4§	143.2§
5	22.6	22.5	3″	127.7	127.4
4-Me	22.6	22.5	4″	108.9	108.9
2′	73.7	72.6	5″	139.3§	139.1§
3′	33.5‡	33.1‡			

*Values taken from ref. [5] for ipomeamarone, a synonym for (+)-ngaione, which has priority in the chemical literature. Note, however, that in ref. [5] the wrong absolute stereochemistry for (+)-ngaione is represented in the structural formula.

†, ‡, § Values with identical superscript may be interchanged.

A sample of 1 in EtOH was treated with 2,4-dinitrophenylsemicarbazide and conc HCl as described [3]. The reaction product was chromatographed on alumina (act. III, neutral). Elution with C_6H_6 gave fractions which crystallized from EtOH–EtOAc as pale-yellow felted needles of the semicarbazone, mp 165–165.5°, $[\alpha]_D - 70°$ (*c* 0.4; $CHCl_3$); lit. [3] mp 166°, $[\alpha]_D - 68°$ (2% in $CHCl_3$).

The portion of the extract insoluble in EtOAc was partitioned between H_2O and CH_2Cl_2. The CH_2Cl_2-soluble fraction (0.8 g) was essentially similar to that extracted with EtOAc. The H_2O-soluble portion was recrystallized from MeOH to give mannitol (100 mg), mp 166–166.5°, $[\alpha]_D - 1°$ (*c* 0.3; H_2O); lit. [7] mp 166°, $[\alpha]_D - 0.21°$. ^{13}C NMR (20.1 MHz, D_2O): δ71.2 (*d*), 69.7 (*d*), 63.5 (*t*).

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*Recent work on the classification of the Myoporaceae has resulted in *M. deserti* being transferred to the *Eremophila* genus [4].