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AN ISOBUTYLAMIDE AND BEYERENE DERIVATIVES FROM *BRACHYCOME* SPECIES

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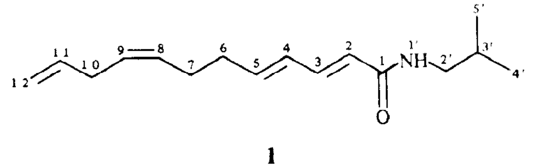
Key Word Index—*Brachycome* species; Compositae; unsaturated amide; diterpenes; beyerene derivatives.

Abstract—The investigation of some *Brachycome* species gave, in addition to widespread compounds, beyerene derivatives and a new highly unsaturated isobutylamide.

The genus *Brachycome*, with 66 species, shows a large variety of chromosome numbers reaching from two to 45. Most of the species are from Australia, but three are from New Zealand and one from New Guinea [1]. Preliminary chemical studies have shown that the roots contain acetylenes typical for the Astereae [2]. We have now studied the aerial parts of a few species. Those of *Brachycome ciliocarpa* W. Fitzg. gave, in addition to germacrene D, bicyclogermacrene, geranyl- and borneyl acetate the amide **1**.

The presence of an isobutylamide followed from the typical ^1H NMR signals [5.48 *br s*, 3.16 *t* (2H), 1.80 *tqq* and 0.92 *d* (6H)]. Furthermore nine low field signals were visible. Accordingly, in addition to a vinyl end group (5.82 *ddt*, 5.03 *ddt* and 4.98 *ddt*) three further double bonds were present. Spin decoupling allowed the assignment of all signals and the observed couplings indicated the configurations. Therefore the structure was assigned in agreement with the fragmentation pattern in the mass spectrum.

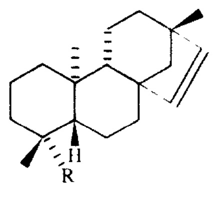


1

The aerial parts of *B. iberidifolia* Benth. gave the beyerene derivatives **2–4**, the latter so far only being isolated from a *Myriocephalus* species [3]. However, beyerene derivatives are also reported from *Nidorella* [4] and *Baccharis* species [5–7] in the tribe Astereae.

Some further species, *B. ciliaris* (Labill.) Less., *B. ciliaris* (Labill.) Less var. *lanuginosa* and *B. trachycarpa* F. Muell. gave no characteristic compounds.

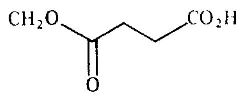
The isolation of the amide **1** is interesting, as so far these highly unsaturated compounds have only been reported in the Compositae from the tribes Anthemideae



2 R = CO_2H

3 R = CH_2OH

4 R =


$CH_2OC(=O)CH_2CH_2CO_2H$

and Heliantheae. However, none of them has a vinyl end group. Accordingly, the amide **1** is formed by a different biogenetic pathway. Further investigations may show whether these amides are of chemotaxonomic importance. So far the chemistry seems to be not very helpful in the case of *Brachycome*.

EXPERIMENTAL

The air-dried aerial parts, collected in August 1986 in W. Australia (vouchers deposited in the US National Herbarium, Washington), were extracted and worked-up as reported previously [8]. The extract of 175 g aerial parts of *B. ciliocarpa* (voucher RMK 9580) gave 10 mg germacrene D, 8 mg bicyclogermacrene, 5 mg geranyl acetate, 7 mg borneyl acetate and 10 mg **1** (TLC: Et_2O, 1 : 1, R_f 0.42); colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3440, 1670, 1560 (CONHR), 1635, 1610, 1000 ($(CH=CH)_2$), 915 ($CH=CH_2$); MS m/z (rel. int.): 247.194 $[M]^+$ (24) (calc for $C_{16}H_{25}NO$: 247.194), 175 $[M-NHCH_2CHMe_2]^+$ (41), 166 $[M-H_2C=CHCH_2CH=CHCH_2]^+$ (37), 81 $[C_6H_9]^+$ (77), 67 $[C_5H_7]^+$ (58), 57 $[C_4H_9]^+$ (100); ^1H NMR ($CDCl_3$, 400 MHz): 5.75 (*br d*, H-2), 7.18 (*dd*, H-3), 6.15 (*dd*, H-4), 6.06 (*dt*, H-5), 2.20 (*m*, H-6, H-7), 5.43 (*m*, H-8, H-9), 2.79 (*br t*, H-10), 5.82 (*ddt*, H-11), 5.03 (*ddt*, H-12t), 4.98 (*ddt*, H-12c), 5.48 (*br s*, NH), 3.16 (*t*, H-2′), 1.80 (*tqq*, H-3′), 0.92 (*d*, H-4′, H-5′); (*J*[Hz]: 2,3 = 14.5; 3,4 = 10; 4,5 = 15; 5,6 = 9,10 = 10,11 = 6; 11,12t = 17; 11,12c = 10; 10,12t = 10,12c = 12c, 12t = 1.5; 1′,2′ = 2′,3′, = 3′,4′ = 3′,5′ = 7).

The extract of 185 g aerial parts of *B. iberidifolia* (voucher RMK 9541) gave 5 mg **2**, 10 mg **3** and 100 mg **4**. The extract of 305 g aerial parts of *B. ciliaris* (voucher RMK 9579) gave 5 mg spathulenol and fatty acids, those of 260 g *B. ciliaris* var. *lanuginosa* (voucher RMK 9614) and 470 g *B. trachycarpa* (voucher RMK 9620) gave fatty acids.

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TETRAPHYLLIN B FROM *ADENIA CISSAMPELOIDES*

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Key Word Index—*Adenia cissampeloides*; Passifloraceae; root cyanogenic glycoside; tetraphyllin B; fish poison.

Abstract—This paper reports the isolation of tetraphyllin B, a cyanogenic glycoside, from *Adenia cissampeloides* roots.

INTRODUCTION

Adenia cissampeloides has been used for fish poisoning [1, 2]. Earlier work on the stem led to isolation of friedelan-3β-ol, friedelan-21-one; sitosterol; 4-methoxycyclopent-2-enone and 4-ethoxycyclopent-2-enone [1]. The alkoxycyclopentenones were shown to be artefacts formed from 4-hydroxycyclopent-2-enone during extraction [1]. Based on the observed cyanogenesis and the occurrence of 4-hydroxycyclopent-2-enone, tetraphyllin B was proposed as the cyanogenic glycoside of *A. cissampeloides*. It has also been shown that tetraphyllin B is the toxic component of an East African homicide poison, *A. volkensii* [3]. Further work on *A. cissampeloides* also led to isolation of succinic acid, mannitol, sucrose and sodium chloride from the stem [4]. The present work reports the isolation of tetraphyllin B from *A. cissampeloides* root. Tetraphyllin B is therefore confirmed as the toxic component of *A. cissampeloides*. The occurrence is also of chemotaxonomic importance since cyanogenic glycosides of the cyclopentene group are restricted to only a few families of the order Parietales.