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.

Cyclopentenoid cyanogenic glycosides have been reported in some other *Adenia* species. For example gynocardin has been suggested as the main cyanogen of *A. lobata* [5] based on qualitative paper chromatographic evidence. *Adenia volkensii* was shown to contain tetraphyllin B and one of its stereoisomers [3]. The stereoisomer was later shown to be volkenin, (1*R*, 4*R*)-1-(β-D-glucopyranosyloxy)-4-hydroxy-2-cyclopentenecarbonitrile [6], which is a diasteroisomer of tetraphyllin B. The bulb of an unspecified *Adenia* species (South African Natural Herbarium No. 7611) was reported [7] to contain cyanogenic glycoside. The leaves of *A. glauca* were also reported to release hydrogen cyanide [7]. Tetraphyllin B and its diastereoisomer, volkenin, were later isolated from *A. glauca* [8] and *A. gracilis* [9]. Spencer *et al.* [10] isolated tetraphyllin B from the South African poisonous plant, *A. digatata* and reported cyanogenesis in an *Adenia* species from Madagascar [11]. Cyclopentenoid cyanogenic glycosides have also been reported in some other members of the Passifloraceae [12–15].

RESULTS AND DISCUSSION

Adenia cissampeloides root collected in late December was extracted with methanol. The concentrate was partitioned between chloroform and water. The water fraction was concentrated and taken into methanol–ethyl acetate and left to stand in a refrigerator. This gave tetraphyllin B as needles, mp 166–168°. The 60 MHz ^{1}H NMR data in D_2O were in accord with the literature values for tetraphyllin B [12]. Acidic hydrolysis of tetraphyllin B afforded 4-hydroxycyclopent-2-enone as an oil λ_{max}^{MeOH} 213 nm, ν_{max} 3350 and 1720 cm^{-1}. The 60 MHz ^{1}H NMR data were in accord with literature value for 4-hydroxyclopent-2-enone [1, 12]. Tetraphyllin B has never been isolated from *A. cissampeloides* before.

EXPERIMENTAL

Isolation of tetraphyllin B. The air-dried, powdered root bark of *A. cissampeloides* (300 g) was defatted with petrol followed by extraction with hot MeOH for five min. The MeOH extract was concd *in vacuo* and partitioned between $CHCl_3$ and H_2O. The H_2O fraction was concd *in vacuo* to a reddish syrup. This was taken into MeOH–EtOAc mixture and left in a refrigerator. On standing overnight it gave tetraphyllin B(**1**) (185 mg), mp 166–168° ^{1}H NMR (60 MHz, D_2O, TMS) δ 6.45 (1H, *dd*, J = 6 Hz, J^1 = 1 Hz); 6.25 (1H, *dd*, J = 6 Hz, J^1 = 1 Hz); 4.95 (1H, m); 2.90 (1H, *dd*, J = 15 Hz, J^1 = 6 Hz) and 2.35 (1H, *dd*, J = 15 Hz, J^1 = 4.5 Hz).

Hydrolysis of tetraphyllin B. Tetraphyllin B (110 mg) was heated with 0.5 M H_2SO_4 (2 ml) on a steam bath for 3.5 hr. The reaction mixture was neutralized with $BaCO_3$ and filtered. The filtrate was concd *in vacuo* and chromatographed over silica gel. Chloroform eluted 4-hydroxy-2-cyclopentenone as an oil (18 mg) λ_{max}^{MeOH} 213 nm (ε 6135); ν_{max} cm^{-1} 3350 and 1720; ^{1}H NMR (60 MHz, $CDCl_3$, TMS) δ 7.50 (1H, *dd*, J = 6 Hz, J^1 = 2.5 Hz); 6.14 (1H, *dd*, J = 6 Hz, J^1 = 2.5 Hz); 4.8 (1H, *m*); 2.65 (1H, *dd*, J = 18 Hz, J^1 = 6 Hz); 2.15 (1H, *dd*, J = 18 Hz, J^1 = 2.5 Hz).

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