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QUINONOID AND OTHER CONSTITUENTS OF *ARISTEA ECKLONII*

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Key Word Index—*Aristea ecklonii*, Iridaceae, quinones, plumbagin, biplumbagin, neoisoshinanolone, sterols

Abstract—Plumbagin, 3,3′-biplumbagin, 8,8′-biplumbagin, neoisoshinanolone and sitosterol were isolated from the leaves and rhizomes of *Aristea ecklonii* The rhizomes also contained α-spinasterol This is the first report of plumbagin, previously found in several dicotyledonous families, in a monocotyledon

INTRODUCTION

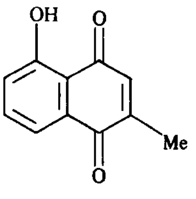
Amino acids, flavones, terpenes and quinones have been reported to occur in members of the Iridaceae [1] The eleven quinones reported include two benzoquinones [2, 3], two naphthoquinones [4] and seven anthraquinones [4, 5], although the need for verification of some of the latter has been commented upon [4] The genus *Aristea*, which contains 40 species mostly found in South Africa [6], has not been previously studied *A ecklonii*, a perennial herb introduced into Sri Lanka and growing abundantly in the higher altitudes of the country, contained plumbagin, two plumbagin derivatives, neoisoshinanolone and two sterols

RESULTS AND DISCUSSION

The dichloromethane extract of *A ecklonii* rhizomes on chromatographic separation yielded three quinones, plumbagin (**1**), 3,3′-biplumbagin and 8,8′-biplumbagin, two sterols, α-spinasterol and sitosterol, and a compound related to isoshinanolone (**2b**) This compound, for which we assign the trivial name neoisoshinanolone, differed markedly from that isolated from *Diospyros maritima* [7] in some of its physical characteristics although it possessed similar spectral and chiroptical properties and was identical to what has been reported as 'isoshinanolone' from *Plumbago zeylanica* [8] Like isoshinanolone (**2b**), neoisoshinanolone (**2a**) could be oxidized to plumbagin (**1**) The coupling constant of the carbinyl proton at C-4 of neoisoshinanolone with the methine proton at C-3 was $J = 2\ 5$ Hz, suggesting that of the methyl and hydroxyl groups, one has an equatorial or a pseudo-equatorial orientation while the other has an axial or a pseudo-axial orientation Tezuka *et al* [7] suggested the stereochemistry of isoshinanolone to be **2b** on the basis of the aromatic chirality method, although they express some doubt on the validity of the method Waterman and co-workers [9] isolated a mixture of isoshinanolone (**2b**) and its 1*S*,2*R*-diastereoisomer **2c** from *Diospyros canaliculata* The coupling constants from ^{1}H NMR suggest H-1 and H-2 in the latter to exist in pseudo-axial and axial orientations However, the assignment of stereochemistry on the basis of comparison of the optical rotation of the mixture with that of shinanolone, which has additional methyl substitution in the aromatic ring, is not entirely unequivocal

The CD curve of the dibenzoate of neoisoshinanolone (**2a**) isolated from *P zeylanica* [8] was found to be similar to that of isoshinanolone [7] The ^{1}H NMR chemical shifts of neoisoshinanolone (**2a**) and isoshinanolone (**2b**) were similar We believe that neoisoshinanolone (**2a**) and isoshinanolone (**2b**) are enantiomeric and one or both may be partly racemized The use of the aromatic chirality method in assigning the stereochemistry of isoshinanolone (**2b**) appears to be questionable The higher optical rotation and the isolation of the identical material from two very different sources, *A ecklonii* and *P zeylanica*, suggest that neoisoshinanolone (**2a**) contains a greater amount of the enantiomer of negative rotation However, the assignment of its stereochemistry will require further work The dichloromethane extract of *A ecklonii* leaves on similar separation was found to contain all the compounds found in the rhizome extract, except for α-spinasterol Plumbagin was the major constituent of both extracts

3,3′-Biplumbagin and 8,8′-biplumbagin have previously been reported only in the roots of *Plumbago zeylanica* [9] and *Diospyros maritima* [10], respectively, which also contain plumbagin Plumbagin, 7-methyljuglone and analogous compounds are found in the Droseraceae, Ebenaceae, Plumbaginaceae and related families [11] *A ecklonii* is the first example of a monocotyledonous plant species containing plumbagin [1]



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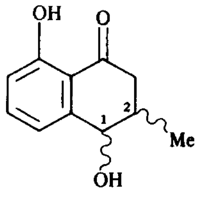

2a 1α, 2α
2b 1β, 2β
2c 1α, 2β

EXPERIMENTAL

Mps were determined on a Kofler hot-stage apparatus and are uncorr Identities of the compounds were established by mmp, IR, mass and NMR comparison Petrol refers to the fraction having a boiling range of 40–60° and prep TLC was carried out on Merck Kiesel gel 60 Optical rotations were measured at 27° in $CHCl_3$ IR spectra were recorded for KBr discs, ^1H NMR spectra were recorded at 60 MHz in CCl_4 with TMS as internal standard

Extraction of plant material The rhizomes and leaves of *A ecklonii* Baker were collected from Nuwara Eliya in central Sri Lanka, a voucher specimen has been deposited at the University herbarium The rhizomes and leaves were dried and ground separately and the powdered material (0 75 and 1 kg, respectively) was extracted at 27° with CH_2Cl_2 twice during two successive 24 hr periods Concn gave a brown solid (9 6 g) and a dark green gum (15 g), respectively

Chromatography of the rhizome extract The rhizome extract (9 g) was chromatographed over silica gel (250 g) using petrol–$CHCl_3$ mixtures as eluants Elution with petrol–$CHCl_3$ (7 3) gave plumbagin (**1**) (1 6 g), yellow needles from hexane, mp 75–77° (lit [10] mp 73°), identical with authentic material Elution with petrol–$CHCl_3$ (1 1) gave a mixture, which was separated by prep TLC (C_6H_6 × 2) to yield the less polar 3,3′-biplumbagin (28 mg), orange needles, mp 215–216° (lit [10] mp 214–216°) and the more polar 8,8′-biplumbagin (19 mg), red crystals from MeOH, mp 193–195° (lit [7] mp 193–195°), whose spectral data were identical with those reported Elution with petrol–$CHCl_3$ (1 4) gave a mixture, which on separation by prep TLC ($CHCl_3$) gave α-spinasterol, mp 165–167°, $[\alpha]_D$ −3 6° (lit. [12] mp 172–175°, $[\alpha]_D$ − 3 7°) and sitosterol, mp 136–137°, $[\alpha]_D$ − 35° (lit [12] mp 136–137°, $[\alpha]_D$ − 35°), identical with authentic material Elution with $CHCl_3$ gave a fraction, which on purification by prep TLC (CH_2Cl_2 × 2) afforded neoisoshinanolone (**2a**) (1 2 g) as a pale yellow semi-solid, $[\alpha]_D$ + 24° Found C, 68 3, H, 6 8 $C_{11}H_{12}O_3$ requires C, 68 7, H, 6 7% UV λ_{max}^{EtOH} nm 217, 259, 335, IR ν_{max} cm^{-1} 3600–3150, 1630, 1570; ^1H NMR ($CDCl_3$) δ1 15 (3H, *d*, $J = 6$ Hz, 2-Me), 1 96–3 15 (4H, *m*, H-2, H-3, OH-1), 4 72 (1H, *d*, J = 2 5 Hz, H-1), 6 8–7 65 (3H, AB_2, H-6, H-7, H-8)

Neoisoshinanolone diacetate Acetylation of neoisoshinanolone (100 mg) with Ac_2O (1 ml) and pyridine (1 ml) gave the diacetate, colourless crystals from MeOH, mp 91–93°, $[\alpha]_D$ + 128 3°, IR ν_{max} cm^{-1} 1760, 1635, 1235, 1200; ^1H NMR δ1 08 (3H, *d*, J = 6 Hz, 2-Me), 2 00 and 2 24 (3H each, *s*, –OCOMe), 2 2–2 7 (3H, *m*, H-2, H-3), 6 01 (1H, *m*, $W_{\frac{1}{2}}$ = 4 Hz, H-1), 6 85–7 65 (3H, *m*, H-6, H-7, H-8), MS *m/z* (rel int) 276 $[M]^+$ (1) 192 (50), 174 (100), 146 (38), 131 (16), and 121 (12)

Oxidation of isoshinanolone (**2b**) Isoshinanolone (50 mg) in dioxane (5 ml) was refluxed with DDQ (20 mg) for 18 hr Work-up followed by prep TLC gave plumbagin (22 mg), mp 75–77°, identical with the plumbagin obtained above

Chromatography of the leaf extract Chromatography of the leaf extract (14 g) on silica gel (450 g) using petrol–$CHCl_3$ mixtures as eluants as before gave plumbagin (3 8 g) 3,3′-Biplumbagin (213 mg), 8,8′-biplumbagin (320 mg) and sitosterol (300 mg) were identical to those obtained from the rhizome extract

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