

(rel. int.) 293 [M]⁺ (C₁₇H₁₁O₄N) (4.6), 279 [M-CH₂]⁺ (100), 264 [M-COH]⁺ (3.5), 250 [M-CO-Me]⁺ (15), 220 (19.2), 206 (25.5), 191 (53.9), 178 (45.1), 151 (16.1).

Rutalpinin **2**, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm 293 (log ε 4.2), 235 (log ε 4.5). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹ 3050, 2950, 2840, 1720 (sh), 1705, 1680 (sh), 1600, 1500, 1480, 1440, 1355, 1240, 1180, 1030, 930, 860, 800. ¹H NMR see text. MS, 70 eV (probe) *m/z* (rel. int.) 258.75 [M]⁺ (C₁₅H₁₄O₄) (75), 243 [M-Me]⁺ (8), 230 [M-CO]⁺ (10), 215 [M-CO-Me]⁺ (10), 135 [C₈H₇O₂]⁺ (100), 105 [C₆H₅O]⁺ (40), 77 [C₆H₅]⁺ (45).

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ALKALOIDS OF *TECLEA NOBILIS*

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Key Word Index—*Teclea nobilis*; Rutaceae; quinoline alkaloids; nobiline; isoplatydesmine; ribalinine; edulinine; montrifoline; skimmianine; flindersiamine; maculine.

Abstract—A new furoquinoline alkaloid to which we have assigned the trivial name nobiline, and seven other quinoline alkaloids were isolated and identified from the leaves and fruits of *Teclea nobilis*, an African medicinal plant.

INTRODUCTION

Teclea nobilis is a rutaceous plant widely distributed in tropical Africa and is known in many African societies as a medicinal plant. In South Africa the bark is reported to be a remedy for gonorrhoea while in Tanzanian folk medicine the leaves are used as cure for fever [1]. Similarly in Ethiopian traditional medicine the bark and leaves are used as analgesics. Although many species of the genus *Teclea* have been investigated for their alkaloidal composition [2, 3], there is no prior report on the chemical constituents of *T. nobilis*. We therefore examined the leaves and fruits of this plant, since preliminary chemical screening showed both to be rich in alkaloids.

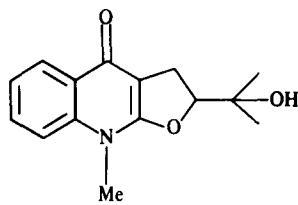
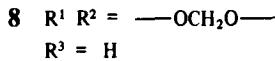
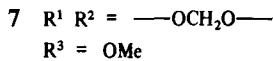
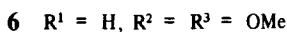
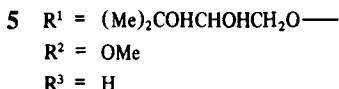
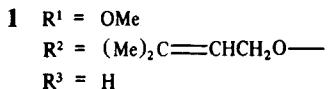
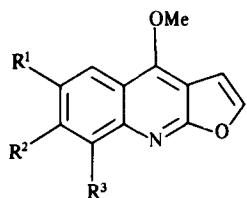
RESULTS AND DISCUSSION

TLC examination of the alkaloidal fraction of the leaves of *T. nobilis* revealed the presence of at least nine alkaloids. Upon silica gel chromatography and crystalliz-

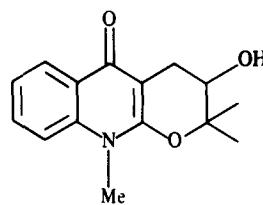
ation a hitherto unreported alkaloid named nobiline (**1**), C₁₈H₁₉NO₄ ([M]⁺ 313), mp 117–119° and seven other known alkaloids were isolated. The identities of the known alkaloids were determined by spectroscopic means and in some cases by comparison with authentic samples.

Spectroscopic evidence, especially UV and NMR, indicated that the new compound was a 4-methoxyfuroquinoline alkaloid. The mass spectrum of compound (**1**) showed in addition to the [M]⁺, significant peaks at *m/z* 298 [M-15]⁺, 284, 245 [(M-68)⁺ 100%) and 230 [M-83]⁺. Loss of a fragment of *m/z* 68 is characteristic of compounds having a prenyloxy moiety. The ¹H NMR spectrum of (**1**) in CDCl₃ showed the presence of two methyl groups appearing as a singlet at δ 1.76, strongly suggesting their attachment to an olefinic functional group, an assignment further supported by signals appearing as a doublet at 4.73 and a triplet at 5.62 ppm caused respectively by methylene protons and an olefinic proton of a dimethylallyloxy side chain. Two OMe groups appear at 4.0 and 4.42 ppm, the latter signal indicative of a methoxy group at C-4, based on chemical shift data reported for 4-methoxyfuroquinoline alkaloids [4]. A pair of AB doublets at 7.04 and 7.58 ppm (*J*=3 Hz) corresponded to the two furan protons, while the two

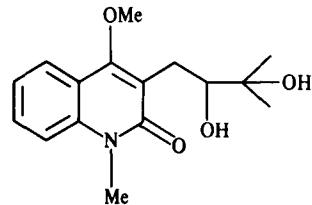
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2



3



4

singlets at 7.36 and 7.49 ppm represented H-8 and H-5 protons, respectively. The positions of the prenyloxy and the normal methoxy groups were established by an NOE study. Irradiation of the OMe group appearing at 4.0 ppm resulted in a 20.7% signal enhancement of H-5 clearly showing that this methoxy group is located at C-6. This then leads to placing the prenyloxy group at C-7.

Isoplatydesmine (2) and ribalinine (3) were readily isolated from both the leaves and fruits of *T. nobilis* and gave rise to spectral characteristics identical to those reported in the literature [5, 6]. The latter compound, by far the most abundant of the *T. nobilis* alkaloids, was identical except with respect to rotation to an authentic sample [6] isolated from *Araliopsis soyauxii*. Varying rotation values have been reported for ribalinine. Ribalinine, first isolated [5] from the Argentinian plant *Balfourodendron riedelianum* was reported to be racemic, whilst a laevorotatory compound was isolated from *A. soyauxii* with $[\alpha]_D - 10^\circ$. Interestingly dextrorotatory ribalinine, $[\alpha]_D + 8^\circ$, was also isolated from *A. tabouensis* [7]. The ribalinine isolated here from *T. nobilis* had an $[\alpha]_D$ of -78° indicating the partial racemic nature of ribalinine obtained from *A. soyauxii*. To our knowledge, this is the first report on the occurrence of compounds (2) and (3) in the genus *Teclea*.

The leaves and fruits of *T. nobilis* also yielded edulinine (4). It has been previously reported that edulinine can be isolated in many instances only under basic conditions and not at neutral or acidic pH values and because of this it has been indicated that it may be an artefact of isolation [8–11]. We could also isolate edulinine only under basic conditions.

The occurrence of the furoquinoline alkaloids montri-

foline (5) skimmianine (6), flindersiamine (7) and maculine (8) in the leaves of *T. nobilis* further attest to how rich this plant is in quinoline alkaloids. These alkaloids were readily identified by spectroscopic methods and, in the case of montrifoline and flindersiamine, by comparison with authentic samples.

EXPERIMENTAL

General. Mps: uncorr. 1H NMR were measured in $CDCl_3$ with TMS as int. std on 90 MHz instruments. The NOE study was conducted on a 360 MHz NMR instrument.

Plant material. *T. nobilis* Delile leaves and fruits were collected from Menagesha, Lepis and Harena State Forests, Ethiopia at altitudes of 2800, 2100 and 1400 m, respectively. The plant was identified by Mr Zemde Asfaw and a voucher specimen is kept at the National Herbarium of Ethiopia (Zemde 535).

Extraction and fractionation. Air-dried finely ground leaves were extracted for 12 hr in a Soxhlet using EtOH; the solvent was removed *in vacuo*. The alkaloid fraction was sep'd from the crude extract by usual methods. TLC of the alkaloidal fraction using $CHCl_3$ –MeOH (9:1) showed the presence of nine alkaloids, which were sep'd by silica gel CC eluting with $CHCl_3$ followed by $CHCl_3$ –MeOH (19:1). Final purification in some cases was achieved by prep. TLC using benzene–EtOAc (4:1).

Nobiline (1). Mp 117–119°; $[\alpha]_D^{24} 0^\circ$ ($CHCl_3$; c 0.1). UV λ_{max}^{OH} nm (log ϵ): 243 (4.7), 249 (4.7), 282 (3.8) sh, 293 (3.9), 307 (4.0), 319 (4.0), 333 (4.5). IR ν_{max}^{KBr} cm $^{-1}$ 3175, 2950, 2890, 1640, 1600, 1519, 1490, 1380, 1330, 1270, 1220, 1100, 840. 1H NMR (see text). MS 70 eV m/z (rel. int.): 313 [M] $^+$, 298, 284, 245 (100), 230 (40).

Isoplatydesmine (2). Mp 189–191° (lit. 191° [6]). $[\alpha]_D^{24} + 50^\circ$

(CHCl₃; *c* 1), (lit. +60° [6]). IR, UV, NMR and MS identical to lit. [6].

Ribalinine (3). Mp 232–234° (lit. 232° [5, 6]). $[\alpha]_D^{24} -78^\circ$ (CHCl₃; *c* 1), (lit. 0° [5], -10° [6]). Other spectroscopic data identical to lit. cited in text.

Edulinine (4). Identified by spectroscopic data and also comparison with authentic sample (co-TLC).

Montrifoline (5). Mp 188–189° (lit. 189–190° [4]). Identified by NMR and MS data; identical with an authentic sample of montrifoline (mmp, co-TLC).

Skimmianine (6). Mp 168–170° (lit. 170–172° [12]), *flindersamine* (7): mp 207–209° (lit. 207–208° [13]) and *maculine* (8): mp 197–199° (lit. 198° [14]) were identified based on their spectroscopic data which were in good agreement with the lit.

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(+)-3',4'-DIHYDROSTEPHASUBINE, A BISBENZYLISOQUINOLINE ALKALOID FROM *STEPHANIA HERNANDIFOLIA*

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Key Word Index—*Stephania hernandifolia*; Menispermaceae; bisbenzylisoquinoline alkaloid; 3',4'-dihydrostaphasubine; staphasubine; epistephanine.

Abstract—A new bisbenzylisoquinoline alkaloid has been isolated from the stems of *Stephania hernandifolia* and its structure established as (+)-3',4'-dihydrostaphasubine. This is accompanied by the known alkaloid (+)-staphasubine (+)-Epistephanine has been found in the roots of the plant.

INTRODUCTION

Recent phytochemical investigation on *Stephania suberosa* [1–3] prompted us to reinvestigate the alkaloid contents of *S. hernandifolia* Walp. We report here the isolation of a new bisbenzylisoquinoline alkaloid, the structure of which has been established as (+)-3',4'-dihydrostaphasubine (1), along with (+)-staphasubine (2)

[1] from the stems of *S. hernandifolia*. (+)-Epistephanine (3) occurs in the roots of the same plant.

RESULTS AND DISCUSSION

Compound 1, C₃₆H₃₆N₂O₆, exhibited a strong [M]⁺ at *m/z* 592 (38%) with *m/z* 591 as the base peak. The fact