Phytochemistry, Vol. 27, No. 3, pp. 959–960, 1988.
Printed in Great Britain.

0031-9422/88 $3.00 + 0.00

QUINOLINE ALKALOIDS FROM THE LEAVES OF *TECLEA SIMPLICIFOLIA*

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(*Received* 17 *August* 1987)

Key Word Index—*Teclea simplicifolia*; Rutaceae; furoquinoline alkaloids; isohaplopine; isohaplopine-3′,3′-dimethylallylether.

Abstract—Seven alkaloids have been isolated from the leaves of *Teclea simplicifolia* of which five were identified as the known compounds skimmianine, montrifoline, ribalinine, isoplatydesmine and edulinine. The two remaining alkaloids appear to be novel and are characterized as isohaplopine (8-hydroxy-4,7-dimethoxyfuroquinoline) and its 3,3-dimethylallylether on the basis of spectral analysis.

INTRODUCTION

In a continuation of studies on Ethiopian Rutaceae [1] we wish to report the results of an examination of the leaves of *Teclea simplicifolia* Verdoorn, a species widespread in tropical East Africa [2]. In the only previous examination of this species Badger *et al.* [3] reported the isolation of lupeol and *N*,*N*-dimethyl-4-methoxyphenylethylamine and suggested that unidentified furoquinolines were probably present.

By column chromatography over silica gel five known alkaloids were isolated. These were identified as the furoquinolines skimmianine (major compound) and montrifoline, the dihydropyranoquinol-4-one ribalinine, the 2-isopropyldihydrofuroquinol-4-one isoplatydesmine and the 2-quinolone edulinine. All were identified by direct comparison with material isolated from *Teclea nobilis* [1].

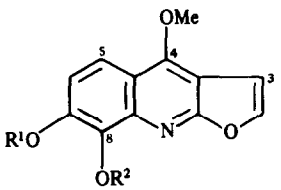
Two further alkaloids were obtained by repeated column chromatography over Sephadex LH20. One of these analysed for $C_{13}H_{11}NO_4$ and had the typical UV spectrum of a phenolic furoquinoline. Its ^{1}H NMR spectrum revealed signals for 2 × OMe, an unsubstituted furan ring and two aromatic protons showing *ortho* coupling, one of which was deshielded, typical of H-5. A highly deshielded methoxyl resonance (δ 4.43) could be assigned to C-4 leaving the second to occupy C-7 or C-8 (e.g. **1** or **2**). Compound **2** is the known alkaloid haplopine [4] and its reported ^{1}H NMR [5] differs from that of the alkaloid isolated here. On this basis this alkaloid must be assigned structure **1**, to which we have given the trivial name isohaplopine. The identity of **1** was confirmed in two ways. First, the ^{13}C NMR spectrum gave OMe resonances at 59.2 ppm (typical for 4-OMe [6]) and 57.2 (acceptable for 7-OMe but not 8-OMe where it would be deshielded due to substituted *ortho* positions [7]). Second, a NOE experiment involving irradiation of the two OMe signals showed strong enhancement of H-3 (due to the 4-OMe) and H-6 (which must be due to the 7-OMe).

The second alkaloid was non-phenolic and analysed for $C_{18}H_{19}NO_4$. The ^{1}H NMR spectrum indicated a furoquinoline with the same substitution pattern and additional signals attributable to a 3,3-dimethylallyloxy substituent. Acid hydrolysis yielded **1** thus allowing assignment of structure **3**, which again appears to be novel. It should be noted that the extraction procedure and initial column chromatography yielded **1** and **3** in a single nonpolar band that was subsequently separated. It seems highly likely that **1** is an artefact derived from **3** during the isolation process.

EXPERIMENTAL

Plant material. Leaves of *Teclea simplicifolia* were collected from the Harenna Forest, Bale Province, Ethiopia, in September 1986. A voucher specimen (S-002) has been deposited at the National Herbarium, Biology Department, Addis Ababa University.

Extraction of alkaloids. Powdered, air-dried leaves (1.2 kg) were extracted in a Soxhlet with EtOH. The extract was concd and partitioned with 2% H_2SO_4. The acid extract was basified with NH_4OH and then partitioned into $CHCl_3$. The resulting $CHCl_3$ extract was subjected to CC over silica gel eluting with



	R¹	R²
1	Me	H
2	H	Me
3	Me	$CH_2CH{=}C(Me)_2$

$CHCl_3$ and then $CHCl_3$ containing increasing amounts of MeOH to give, in order of elution, a mixture, skimmianine (major alkaloid), and edulinine, montrifoline, ribalinine and isoplatydesmine (all in trace amounts only). The mixture was subjected to further CC over Sephadex LH-20 eluting with $CHCl_3$–MeOH (1:1) to give **3** (30 mg) followed by **1** (16 mg).

Identification of alkaloids. Skimmianine, montrifoline, ribalinine, isoplatydesmine and edulinine were all characterised by direct comparison (co-TLC, HPLC, UV) with authentic materials obtained from *Teclea simplicifolia* [4].

Isohaplopine (**1**). Plates from Me_2CO–petrol, mp 121–123°. Found: 245.0690; $C_{13}H_{11}NO_4$ requires 245.0688. UV λ_{max} nm: 247, 325 (+NaOH) 263, 344; IR ν_{max} cm^{-1}: 3300, 1640, 1600, 1520, 1300. ^1H NMR (90 MHz, $CDCl_3$) δ: 7.74 (1H, *d*, *J* = 9 Hz, H-5), 7.56 (1H, *d*, *J* = 2 Hz, H-2), 7.40 (1H, *br s*, 8-OH), 7.22 (1H, *d*, *J* = 9 Hz, H-6), 7.06 (1H, *d*, *J* = 2 Hz, H-3), 4.43 (3H, *s*, 4-OMe), 4.04 (3H, *s*, 7-OMe). ^{13}C NMR (22.5 MHz, $CDCl_3$) ppm: 163.3 (C-8b), 157.7 (C-4), 145.0, 144.5 (C-8a, C-7), 142.8 (C-2), 138.4 (C-8), 114.0 (C-3a), 113.1, 112.8 (C-5, C-6), 105.3 (C-3), 102.4 (C-4a), 59.2 (4-OMe), 57.2 (7-OMe). EIMS *m/z* (rel. int.): 245 $[M]^+$ (100), 244 (22), 230 (38), 227 (83), 216 (19), 202 (33). NOE (360 MHz, $CDCl_3$): irradiation of δ 4.43 signal—enhancement of H-3 (10.6%) and H-5 (1.6%); irradiation of δ 4.04—enhancement of H-6 (11.5%).

Isohaplopine 3′,3′-dimethylallylether (**3**). Plates from MeOH–hexane, mp 118–119°. Found: 313.1301; $C_{18}H_{19}NO_4$ requires 313.1314. UV λ_{max} nm: 247, 323. IR ν_{max} cm^{-1}: 1630, 1600, 1500, 1300, 1250. ^1H NMR (90 MHz, $CDCl_3$) δ: 5.80 (1H, *t*, *J* = 7 Hz, H-2′), 4.80 (2H, *d*, *J* = 7 Hz, O–CH_2-1′), 4.40 (3H, *s*, 4-OMe), 4.00 (3H, *s*, 7-OMe), 1.73, 1.70 (2 × 3H, 2 × *s*, 3′-Me_2). EIMS *m/z* (rel. int.): 313 $[M]^+$ (7), 245 (100), 244 (14), 230 (30), 227 (82), 216 (24), 202 (18), 69 (10).

Acknowledgements—The authors extend their thanks to Mr M. Gilbert, Royal Botanic Gardens, Kew, for identification of the plant material and Dr D. Reed, Department of Chemistry, University of Edinburgh for the NOE spectrum. Financial support from SAREC (Sweden) is acknowledged.

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Phytochemistry, Vol. 27, No. 3, pp. 960–962, 1988.
Printed in Great Britain.

0031-9422/88 $3.00 + 0.00

PYRROLIZIDINE ALKALOIDS FROM *HELIOTROPIUM CURASSAVICUM*

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(*Received* 29 *June* 1987)

Key Word Index—*Heliotropium curassavicum* var. *argentinum*; *H. curassavicum* var. *curassavicum*; Boraginaceae; pyrrolizidine alkaloids; 9-(3′-isovaleryl)viridifloryl retronecine; 9-(3′-acetyl) viridifloryl retronecine.

Abstract—*Heliotropium curassavicum* var. *argentinum* and var. *curassavicum* have been investigated chemically and a new pyrrolizidine alkaloid has been isolated from both. The latter variety also yielded a related acetylated, 9-(3′-isovaleryl)viridifloryl retronecine alkaloid. The structures have been established by spectroscopic means. Trachelanthamidine was the dominant base found in previous studies of *H. curassavicum* whereas retronecine is the necine present in the alkaloids now reported.

INTRODUCTION

In the course of the systematic investigation of pyrrolizidine alkaloids carried out in our laboratory, we have reported the isolation of several from *Senecio* species [1–4]. The present paper deals with the results obtained from the chemical examination of pyrrolizidine alkaloids in *Heliotropium curassavicum* that grows in the Cuyo Region of Argentina. This species is a glaucous fleshy herb that grows in saline areas. The powdered roots have been used by the Indians of the American south-west to apply to sores and wounds [5]. It is sold in Argentina as a medicine recommended for the treatment of rheumatism, gout, arteriosclerosis and to improve blood circulation.

Although several collections of *H. curassavicum* have been made for chemical investigation in different parts of the world there are considerable differences in the results