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ALKALOIDS AND COUMARINS FROM ROOTS OF *RUTA CHALEPENSIS*

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Key Word Index—*Ruta chalepensis*; Rutaceae; root alkaloids; chaloridone; coumarins; rutalpinin.

Abstract—The root extract of *Ruta chalepensis* yielded a new alkaloid chaloridone in addition to skimmianine, kokusaginine and graveoline as well as a new coumarin rutalpinin together with chalepin and chalepensin. The structures of the known and the new compounds were established by spectral methods.

INTRODUCTION

In an earlier study on the aerial parts of *Ruta chalepensis* [1] we have obtained the alkaloids kokusaginine, skimmianine, arboririne, γ-fagarine, graveoline and the new alkaloid 3′-hydroxygraveoline as well as the coumarins chalepensin, chalepin, rutamarin, bergapten, isopimpinellin and xanthatoxin. In the present study, the roots of the same plant yielded kokusaginine, skimmianine and graveoline in addition to a new acridone alkaloid, chaloridone, [4,5-dioxymethylene-11-methylfuro(2,3-*c*)acridin-6 (11H)-on]. Chalepensin was the main compound in the roots and chalepin was also obtained together with a new coumarin, rutalpinin, [4-(1,1-dimethylallyl)-7,8-dioxymethylene coumarin]. The structures were established by spectral methods and by comparison with authentic samples for the known compounds.

RESULTS AND DISCUSSION

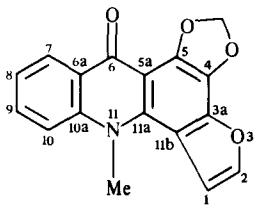
The mass spectrum of chaloridone (**1**) indicated a molecular formula $C_{17}H_{11}O_4N$([M]$^+$, *m/z* 293, 4.6%). The ^{1}H NMR spectrum of **1** showed typical peaks for acridone alkaloids [2–4]. The peaks at δ8.2 (1H, *br d*, $J = 8.1$ Hz, H-7), 7.45 (1H, *t*, $J = 8.1$ Hz, H-8), 7.70 (1H, *dd*, $J = 8$ Hz and 8.1 Hz, H-9) and 7.6 (1H, *dd*, $J = 8$ Hz and 2 Hz, H-10) indicated that ring A has no substitution, those at δ7.55 (1H, *d*, $J = 2$ Hz, H-2) and 7.08 (1H, *d*, $J = 2$ Hz, H-1) showed the presence of a furan ring and the singlet at δ6.00 (2H, *s*) indicated the presence of a dioxymethylene group. Since the N–Me group is at lower field at δ4.10 the furan ring should be situated at C-11b–C-3a as is the case in furoacridon [3]. When the dioxymethylene group is in this position the N–Me signal is observed at δ3.97 [5]; therefore the dioxymethylene group can only be at C-4–C-5. ^{13}C NMR, UV and IR spectra correlated the structure.

The mass spectrum of rutalpinin (**2**) indicated a molecular formula $C_{15}H_{14}O_4$ ([M]$^+$, *m/z* 258.75). The ^{1}H NMR spectrum showed the structure clearly signals at δ1.40 (6H, *s*, 2 × Me), 4.95 (1H, *dd*, $J = 10$ Hz and 1.2 Hz), 6.00 (1H, *dd*, $J = 17$ Hz and 1.2 Hz), 5.20 (1H, *d*, $J = 17$ Hz and 10 Hz) indicated a 1,1-dimethylallyl group, together with those at δ5.95 (2H, *s*, $-OCH_2O-$), 6.64 (1H, *s*, H-3), 6.56 (1H, *d*, $J = 8$ Hz, H-6) and 6.70 (1H, *d*, $J = 8$ Hz, H-5).

EXPERIMENTAL

Roots of *R. chalepensis* L. were collected together with aerial parts from Sedef adasi (Pearl island) near Istanbul in July 1984. Dried and powdered roots (900 g) were extd with $CHCl_3$ in a Soxhlet, the extract evapd under vacuum to yield 19 g of a residue, which was fractionated in a silica gel column. The following compounds were obtained, kokusaginine (10 mg), skimmianine (15 mg), graveoline (8 mg), chaloridone (12 mg), chalepensin (150 mg), chalepin (8 mg) and rutalpinin (4 mg).

Chaloridone **1**. UV λ_{max}^{MeOH} nm 387 (log ε 3.8), 320 (log ε 4.4), 270 (log ε 4.8), 240 (log ε 4.5), 224 (log ε 4.4). IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3080, 2950, 1630, 1580, 1550, 1505, 1500, 1485, 1440, 1410, 1370, 1350, 1240, 1160, 1110, 1035, 985, 930, 880, 830, 810, 760. ^{1}H NMR, see text. ^{13}C NMR ($CDCl_3$) 110.1 (C-1), 144.0 (C-2), 164.1 (C-3a), 158.2 (C-4), 163.1 (C-5), 106.1 (C-5a), 182.2 (C-6), 118.0 (C-6a), 127.2 (C-7), 121.6 (C-8), 133.4 (C-9), 114.6 (C-10), 140.2 (C-10a), 42.5 (N–Me), 142.3 (C-11a), 101.4 ($-OCH_2O-$). MS, 70 eV (probe) *m/z*



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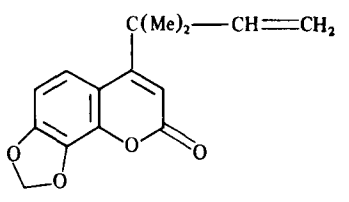

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(rel. int.) 293 $[M]^+$ ($C_{17}H_{11}O_4N$) (4.6), 279 $[M-CH_2]^+$ (100), 264 $[M-COH]^+$ (3.5), 250 $[M-CO-Me]^+$ (15), 220 (19.2), 206 (25.5), 191 (53.9), 178 (45.1), 151 (16.1).

Rutalpinin **2**, UV λ_{max}^{MeOH} nm 293 (log ε 4.2), 235 (log ε 4.5). IR $\nu_{max}^{CHCl_3}$ 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 (proble) *m/z* (rel. int.) 258.75 $[M]^+$ ($C_{15}H_{14}O_4$) (75), 243 $[M-Me]^+$ (8), 230 $[M-CO]^+$ (10), 215 $[M-CO-Me]^+$ (10), 135 $[C_8H_7O_2]^+$ (100), 105 $[C_6H_5O]^+$ (40), 77 $[C_6H_5]^+$ (45).

REFERENCES

1. Ulubelen, A., Terem, B., Tuzlacı, E., Cheng, K. F. and Kong, Y. C. (1986) *Phytochemistry* **25**, 2692.
2. Reisch, J., Rozsa, Zs., Szendrei, K., Novak, I. and Minker, E. (1976) *Phytochemistry* **15**, 240.
3. Reisch, J., Mester, I., Kapoor, S. K., Rozsa, Z. and Szendrei, K. (1981) *Ann. Chem.* 85.
4. Mitaku, S., Skaltsounis, A.-L., Tillequin, F., Koch, M., Pusset, J. and Chauviere, G. (1985) *J. Nat. Prod.* **49**, 1091.
5. Tillequin, F., Baudouin, G., Koch, M. and Svenet, T., (1980) *J. Nat. Prod.* **43**, 498.

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ALKALOIDS OF *TECLEA NOBILIS*

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(*Received* 7 *May* 1987)

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 quinonline 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 crystallization a hitherto unreported alkaloid named nobiline (**1**), $C_{18}H_{19}NO_4$ ($[M]^+$ 313), mp 117–119° and seven other known alkaloids were ioslated. 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 $CDCl_3$ showed the presence of two methyl groups appearing as a singlet at δ1.76, 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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