

which were further confirmed by superimposable IR with the respective authentic samples. Based on the above spectral characteristics and reactions structure **1a** may be assigned to marsupol.

In the mass spectrum of marsupol, the prominent ions m/z 123 (100%) and m/z 137 (30%), may be considered to have been formed by the symmetrical cleavage (shown by the dotted lines in structure **1a**) of the molecule. EIMS (probe) 70 eV m/z (rel. int.); 260 $[M]^+$ (85), 242 $[M - H_2O]^+$ (5), 137 $[M - 123]^+$ (30), 123 $[M - 137]^+$ (100), 119 $[M - 123 - H_2O]^+$ (30), 91 $[M - 123 - H_2O - CO]^+$ (50). The position (δ 2.6) and the broadening of the methyl signal in the NMR spectrum of marsupol may be attributed to the deshielding [6] and the varying eclipsing [4] effects, respectively, caused by the β -OH group.

The structure of marsupol has been confirmed by the synthesis of its dimethyl ether (**1b**) as follows. The required α -methylstilbene (**3**), mp 123° (lit. [7] mp 124°), was prepared by the Grignard reaction between *p*-methoxybenzyl magnesium chloride and *p*-methoxacetophenone; and the subsequent dehydration of the resulting alcohol (**2**), mp 60° (lit. [7] mp 62°), using ethanolic HCl. **3** on reaction with aq. potassium permanganate under phase transfer catalysis conditions [8] using triethylbenzylammonium chloride (TEBAC) as a catalyst, yielded a racemic glycol which was found to be identical with

the dimethyl ether of marsupol (**1b**) (mp, and superimposable IR).

The structure of marsupol may be considered as closely related to angolensin [9], an isoflavonoid isolated from *Pterocarpus angolensis*.

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FURTHER FUROQUINOLONE ALKALOIDS FROM *RUTA CHALEPENSIS**

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Abstract—Two new alkaloids, 9-ethyl-8-methoxy-furo[2,3]quinol-4-one and 9-ethyl-7,8-dimethoxy-furo[2,3]quinol-4-one, and the known furocoumarin chalepin were isolated from *Ruta chalepensis*.

In a recent publication[1], we described the isolation and structure elucidation of taifine (**1**), the first representative of a *N*-ethylfuroquinolone alkaloid. We wish now to report on two further members of

this class, viz. isotaifine (**2**) and 8-methoxytaifine (**3**) also isolated from *Ruta chalepensis* L.

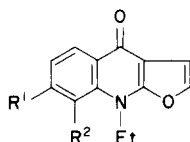
As shown by exact mass measurements, **2** has an elemental composition of $C_{14}H_{13}NO_3$ and is, therefore, an isomer of **1**. Its mass and UV spectra are very similar to those of **1**. The NMR spectrum (see Table 1) differs from that of **1**: the pattern is typical

*Part 14 in the series "Constituents of Local Plants". For Part 13, see ref. [1].

Table 1. NMR spectra of 1-3 (δ ppm, J Hz, multiplicity). The integrals correspond to the number of protons in the structural elements (solvent CDCl_3)

Position	1	2	3
C-2/C-3	7.00; 7.65 3, <i>d</i>	7.02; 7.67 3, <i>d</i>	6.98; 7.60 3, <i>d</i>
C-5	8.00 9, <i>d</i>	7.93 8 and 2, <i>dd</i>	8.10 10, <i>d</i>
C-6	7.38 9 and 3, <i>dd</i>	7.40 8 and 8, <i>t</i>	7.27 10, <i>d</i>
C-7	—	7.09 8 and 2, <i>dd</i>	—
C-8	7.60 3, <i>d</i>	—	—
OCH_3	3.97, <i>s</i>	4.10, <i>s</i>	4.03 and 4.13, <i>s</i>
NCH_2CH_3	4.77 7, <i>q</i>	4.75 7, <i>q</i>	4.75 7, <i>q</i>
NCH_2CH_3	1.63 7, <i>t</i>	1.60 7, <i>t</i>	1.57 7, <i>t</i>

for three neighbouring aromatic protons, one of which (C-5), as in the case of 1, is shifted downfield due to the deshielding effect of the carbonyl group at C-4. As observed for 1 upon addition of CF_3COOH , the ethyl- CH_2 signal is shifted downfield by $\delta 0.25$, because of the protonation of the nitrogen, while the CH_3 -signal remains unchanged. Hence, the ethyl group has to be bound to the nitrogen.



- 1 $\text{R}^1 = \text{OMe}$, $\text{R}^2 = \text{H}$
 2 $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{OMe}$
 3 $\text{R}^1 = \text{R}^2 = \text{OMe}$

Compound 3 has an elemental composition of $\text{C}_{15}\text{H}_{15}\text{NO}_4$. The UV spectrum resembles those of 1 and 2 while in the mass spectrum the fragments in the upper mass region are shifted by $30 \mu\text{m}$ which suggests the presence of a further methoxyl group in 3. This is confirmed (see Table 1) by the presence of two 3H-singlets the positions of which correspond to those in 1 and 2, and the change of the pattern of the hydrogens in the benzene ring which now corresponds to two adjacent protons, one of them at C-5 (*vide supra*).

From the non-alkaloid fraction, a furocoumarin was isolated which, by comparison with the published [2] data, is identical with chalepin.

EXPERIMENTAL

Plant material. The plant was identified by Prof. L. Boulos, National Research Centre, Cairo, and a voucher is deposited in the Herbarium of King Abdulaziz University, Jeddah.

Isolation. From the chromatography on neutral alumina as described in ref. [2] following the elution of taifine (1) further fractions were obtained: (4) C_6H_6 ; 5 mg of a compound mp 102° which could not yet be identified. (5) C_6H_6 with 0.5% CH_3OH ; 30 mg 2; and subsequently 10 mg 3. From the aq. residue obtained after treatment of the crude extract with KOH and extraction with ether [1] after acidification with HCl and extraction with CHCl_3 , chalepin was obtained (mp $117\text{--}120^\circ$, MW: 314, 1536; calcd 314, 1518 for $\text{C}_{19}\text{H}_{22}\text{O}_4$; other data as in ref. [2]).

Isotaifine (2). Needles, mp (from petrol ether) $123\text{--}125^\circ$. IR (KBr): 1620, 1580, 1550, 1515, 1415, 1375, 1355, 1330, 1305, 1270, 1160, 1100, 1025, 995, 750 cm^{-1} . UV (CH_3OH): 243 (4,26), 257 (sh), 267 (sh), 300 (sh), 310 (3,32), 324 (3,31), 338 (3,26) nm (log ϵ). The compound shows violet fluorescence. NMR: see Table 1. MW (mass spectroscopically) 243.0892 (calcd 243.0895 for $\text{C}_{14}\text{H}_{13}\text{NO}_3$).

8-Methoxytaifine (3). Needles, mp (from petrol ether) $122\text{--}123^\circ$. IR (KBr): 1620, 1580, 1555, 1500, 1490, 1420, 1380, 1355, 1295, 1270, 1245, 1115, 1095, 1060, 1020, 990, 740 cm^{-1} . UV (CH_3OH): 248 (4,25), 318 (3,36), 325 (sh), 340 (sh). The compound shows blue fluorescence. NMR: see Table 1. MW (mass spectroscopically) 273.0987 (calc 273.1001 for $\text{C}_{15}\text{H}_{15}\text{NO}_4$).

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