être l'alcaloïde le plus typique des *feuilles* des représentants du genre *Hunteria*. Les diverses espèces se distinguent assez nettement par la nature des autres alcaloïdes présents dans les feuilles *H. corymbosa* [9], *H. umbellata* [10, 11] et *H. eburnea* [3].

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THE CO-OCCURRENCE OF RUTACRIDONE AND NORACRONYCINE IN THE ROOTS OF *BOENNINGHAUSENIA ALBIFLORA*

Zs. Rózsa, K. Szendrei, Z. Kovacs, I. Novák, E. Minker and J. Reisch

Department of Pharmacognosy and Department of Pharmacodynamics, Medical University, Szeged, Hungary and Institute of Pharmaceutical Chemistry, Westfalian Wilhelm University, Münster, FRG

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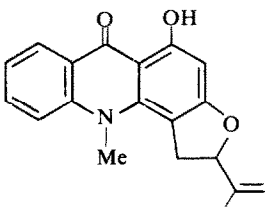
Key Word Index—*Boenninghausenia albiflora*; Rutaceae; acridone alkaloids; rutacridone; 1-hydroxyacridone; 1-hydroxy-*N*-methylacridone; 1,7-dihydroxy-*N*-methylacridone; acridone glycoside.

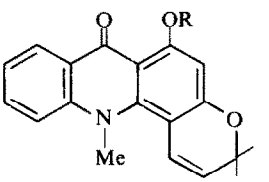
TLC analysis of the methanolic extracts of *Boenninghausenia albiflora* Reichb. revealed the presence of several acridone alkaloids in the roots [1, 2]. Since no acridone alkaloids have been reported from this plant before, solvent–solvent fractionation was undertaken for the separation of these compounds [3]. In a preliminary communication [4] the isolation of three of these yellow alkaloids was described. One of them (Br_3) was identified as 1-hydroxy-*N*-methylacridone (**5**), the two, remaining one were tentatively designated Br_2 and Br_4. In the present paper we report on the characterisation of these two compounds and on three further compounds isolated from the same extract. Two of them (Br_5 and Br_6) were isolated from the benzene soluble fraction of the extract (see Experimental), the third one (Br_7) was separated from the ethyl acetate soluble fraction.

Two (Br_5 and Br_6) were identified by direct comparison with authentic samples as rutacridone (**1**) and noracronycine (**2**) respectively. The alkaloid Br_2, $C_{13}H_9O_2N$ (M^+ at *m/e* 211), in its NMR spectrum indicates the presence of a chelated C-1-OH group and of seven aromatic protons. This region shows a striking similarity to that of *N*-methylacridone. Thus structure **4** (1-hydroxyacridone) can be formulated and this is confirmed by the conversion of **4** to 1-hydroxy-*N*-methylacridone (**5**) via methylation.

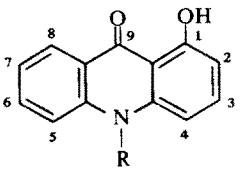
The molecular ion of Br_4 (*m/e* 241) indicates a molecular formula $C_{14}H_{11}O_3N$. The NMR spectrum exhibits two singlets at 3.93 and 14 (C-1-OH) ppm. The assignment of the first mentioned signal to a methylimino-group is deducible from its downfield shift in



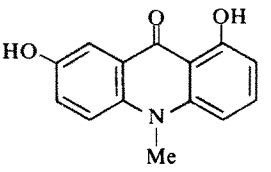
(1)



(**2**): R = H
(**3**): R = Me



(**4**): R = H; (**5**): R = Me



(**6**): Me

trifluoroacetic acid. The brown colour reaction of Br_4 with alcoholic ferric chloride [4] is characteristic for a free phenolic OH-group. An ABX-system analogous to those of Br_2 and Br_3 shows three adjacent protons in position 2, 3 and 4. The remaining signals of the other three protons must be assigned to the second benzene ring. On this basis, structure **6** is favoured. This structural proposal was confirmed by synthesis [5].

Compound Br_7 is slightly water-soluble. Its IR spectrum exhibits very intense OH bands at 3400 and 1060 cm^{-1} indicating its polyhydroxylated nature. Acidic

hydrolysis of Br_7 yielded glucose and a yet unknown acridone aglycone. Thus compound Br_7 must be an acridone glucoside.

To our knowledge, this is the first report on the isolation of 1-hydroxyacridone and of 1,7-dihydroxy-*N*-methylacridone (**6**) from a plant species; compound Br_7 is probably a new natural acridone alkaloid, too.

The most interesting feature of our results is the joint occurrences of rutacridone (**1**) and noracronycine (**2**) in the same plant. To our knowledge *Boenninghausenia albiflora* is the second rutaceous species known to contain both furanoid and pyranoid derivatives in the acridone series. The only other species containing both types is *Atlantia ceylanica*; either furanoid or pyranoid acridones occur in other species, e.g. *Acronychia baueri*, *Glycosmis pentaphylla*, *Atalantia monophylla* and *Ruta graveolens* [6–8].

EXPERIMENTAL

Plant material was collected in May 1974 in the vicinity of Pankhasari, India. The mps of the compounds are uncorr. For the chromatographic separation of the components 70–230 mesh Si gel, Merck TLC Si gel and polyamide were used.

Isolation. 1100 g dried root material was extracted at room temp. with MeOH. The MeOH extract was concd *in vacuo* to 500 ml, diluted with equal vol. of H_2O and extracted with C_6H_6 and EtOAc successively. After evapn of the solvents both fractions were chromatographed on polyamide. The C_6H_6 fraction, when eluted with MeOH–H_2O (3:2) afforded an acridone mixture consisting of three major components (Br_2, Br_3, Br_4) They were further separated on preparative Si gel TLC (C_6H_6, C_6H_6–EtOAc 19:1 and 4:1 systems) then on Sephadex LH 20 columns

Br_2 = *1-hydroxyacridone* (**4**). Mp 280° (subl. decom.), yellow needles from acetone. UV_{max} (MeOH): 241 (infl.) 255 (infl.), 260, 303, 314, 400 nm IRν_{max} (KBr): 3100, 2950, 1640, 1600, 1530, 1470, 1280, 1230, 930, 770 cm^{-1}, see also [4]. NMR ($(CD_3)_2CO$): 14.0 (1H*s*; C-1-OH), 8,3 (1H *q*, H-8), 7.8-7.1 (4H complex *m*, H-3, H-5, H-6 *a*. H-7), 6,9 and 6.5 ppm (each 1H *q* ($J_{A,B}$ = 8 c/s) H-4, H-2). MS: *m/e* 211 (100) (M^+), 183 (29), 154 (31), 127 (12.5). 105 5 (4), 91.5 (14), 77 (31). 1 mg **3** was dissolved in dry Me_2CO and added to a mixture of dry K_2CO_3 in MeI. The mixture was kept at room temp for one day, then filtered and evapd. The product was identified as 1-hydroxy-*N*-methylacridone (**5**) on Si gel and polyamide TLC Systems: C_6H_6–EtOAc (4:1): toluene–EtOAc–HCO_2H (5·4.1): MeOH–H_2O (3:1).

Br_3 = *1-hydroxy-N-methylacridone* **5**. mp, mmp, UV and IR data see [4] MS: *m/e* 225 (100, M^+), 210 (3), 197 (7.5), 196 (7), 182 (16), 168 (3.5), 167 (3), 154 (5), 127 (4), 112.5 (2), 98 5, 77 (6).

Br_4 = *1,7-dihydroxy*-N-*methylacridone* (**6**) mp 308° (subl., decom.) yellow needles from acetone. UV_{max} (MeOH): 244 (infl), 262, 272, 314 (infl), 328 (infl.), 410 nm IRν_{max} (KBr): 3250, 2900, 1635, 1590, 1520, 1480, 1280, 1230, 810, 765 cm^{-1}, see also [4]. NMR ($(CD_3)_2CO$) 14.0 (1H *s*; C-1-OH), 7.75 (1H *d* (*J* = 2 c/s; H-8), 7 -7.5 (3H, complex *m*, H-3, H-5, H-6), 6.9 (1H *q*,($J_{A,B}$ = 8 c/s) H-4), 6 5 (1H *q*, ($J_{A,B}$ = 8 c/s), H-2) and 3.93 ppm (3H *s*, Me—N<, in trifluoroacetic acid 4.10 ppm) MS: *m/e* 241 (100, M^+), 226 (67), 212 (8.5), 193 (15), 183 (2), 170 (18), 154 (3,5), 142 (9), 141 (8.5), 140 (8), 120.5 (19), 115 (11.5), 85 (7.5), 77 (9) The fractions eluted with MeOH–H_2O (4:1) contained two yellow compounds (Br_5 and Br_6). These substances were separated on PLC (C_6H_6–EtOAc (19:1)) and were further purified on Sephadex LH 20 column [4].

Br_5 = *rutacridone* (**1**). mp 162–164° (lit 161 162°) mmp 162–164° yellow needles from Me_2CO–petrol Co-chromatography on Si gel and polyamide layers gave identical R_f-values with those of authentic rutacridone. MS: *m/e* 307 (100, M^+), 292 (30), 278 (29), 264 (27), 250 (16), 239 (16), 236 (15), 222 (6), 208 (12), 183 (4), 180 (6.5), 167 (5), 154 (5), 146 (2), 140 (5), 127 (1), 115 (1,2), 107 (9), 89 (3, 5), 77 (13).

Br_6 = *noracronycine* **2**. mp 200–204°, (lit. 198–200°), mmp 203–205° orange crystals from C_6H_6. UV λ_{max} 250, 260 (*sh*), 275, 301, 335 (*sh*), 405 nm. IR ν_{max} 3400, 2930, 1620, 1590, 1500, 1460, 1410, 1060 cm^{-1}. Co-chromatography on Si gel and polyamide TLC gave identical R_f-values with those of the authentic noracronycine. 0.5 mg **2** was dissolved in dry Me_2CO and added to a soln of dry K_2CO_3 in Me_2SO_4. The mixture was kept at room temp. for one week. The product was identified as acronycine **3** on Si gel and polyamid TLC.

Br_7 = *acridon-glucoside* Mp 167–177° amorphous powder from EtOAc–MeOH 17 mg of Br_7 was refluxed on a stream bath in NH_2SO_4 for 1 hr The mixture was then neutralized with $BaCO_3$, filtered, washed and extracted with EtOAc. In the neutralized aq. layer glucose was identified by PC. 13 mg Br_7 were acetylated at room temp. with Ac_2O–Py. The acetate was obtained as yellow crystals, mp 160–165 .

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