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QUINOLINE AND INDOLOPYRIDOQUINAZOLINE ALKALOIDS FROM *VEPRIS LOUISII*

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Key Word Index—*Vepris louisii*; Rutaceae; stem bark; alkaloids; 2-quinolones; veprisine; *N*-methylpreskimmianine; indolopyridoquinazoline; 1-hydroxyrutaecarpine; 7,8-dehydro-1-hydroxyrutaecarpine.

Abstract—The structures of two new 2-quinolone alkaloids from the stem bark of *Vepris louisii*, *N*-methylpreskimmianine [7,8 - dimethoxy - 3 - (3 - methylbut - 2 - enyl) - 1 - methyl - 2 - quinolone] and veprisine (7,8 - dimethoxy - *N* - methylflindersine) have been deduced from their spectral data and confirmed by partial synthesis from known compounds. Two minor indolopyridoquinazoline alkaloids were also isolated and identified as the already known 1-hydroxyrutaecarpine and the hitherto unknown 7,8-dehydro derivative of 1-hydroxyrutaecarpine.

INTRODUCTION

Recently we reported on the isolation of limonin and a new quinoline alkaloid with an unusual oxygenated prenyl group, veprisilone, from the polar extracts of the stem bark of *Vepris louisii* [2]. Chromatography of the combined hexane and chloroform extracts has now yielded lupeol and two new 2-quinolone alkaloids: *N*-methylpreskimmianine (**1**) and veprisine (7,8-dimethoxy-*N*-methylflindersine) (**3**). In addition, we isolated two minor indolopyridoquinazolines, 1-hydroxyrutaecarpine (**11**) and its 7,8-dehydro derivative (**12**). The structures of **1**, **3**, **11** and **12** and their derivatives have been determined by ^{1}H NMR spectroscopy, chemical interconversions and, in some cases, by unambiguous partial syntheses.

RESULTS AND DISCUSSION

N-Methylpreskimmianine (**1**) $C_{18}H_{23}O_4N$ had IR and UV spectral characteristics of a 2-quinoline [2,3] and its structure was deduced as 7,8-dimethoxy - 3 - (3 - methylbut - 2 - enyl) - 1 - methyl - 2 - quinolone from its ^{1}H NMR spectrum [1]. Confirmation of structure **1** was obtained by partial synthesis of **1** from preskimmianine (**2**), previously totally synthesized by Storer and Young [4]. The second alkaloid, veprisine (**3**) $C_{17}H_{19}O_4N$, also showed characteristic IR and UV spectral absorptions of a 2-quinolone. The UV spectrum in particular resembled that of oricine (**4**) [5]. A detailed analysis of the ^{1}H NMR spectrum of veprisine suggested **3** for its structure, which was confirmed by partial synthesis. *N*-Methylpreskimmianine (**1**) was simultaneously demethylated and cyclized with boiling conc. hydrochloric acid. Dehydrogenation of the resulting reaction mixture, comprising the angular (**5**) (4%) and the linear (**6**) (86%) tetrahydropyranoquinolines, with DDQ then gave veprisine (**3**) identical (IR, ^{1}H NMR, mmp) with the natural sample. The isolation of **3** as the only product of the above dehydrogenation reaction supports the suggestion of Maat *et al.* [6] and Grundon *et al.* [7] that only the pyrano ring opens during treatment with DDQ.

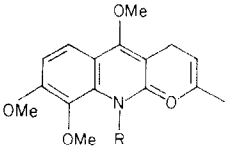
The availability of adequate amounts of *N*-methylpreskimmianine (**1**) prompted us to prepare some of its derivatives and to attempt a synthesis of isoskimmianine (**10**) [8]. Thus oxidation of **1** with *m*-chloroperoxybenzoic acid in chloroform at room temperature followed by treatment with aqueous 2 N NaOH afforded the diol (**7**). Treatment of **7** with hot dilute H_2SO_4 at 80° furnished a new compound which showed ν_{max} at 1655 cm^{-1}. From the mass and NMR spectra, and by analogy with similar [9] acid-catalysed cyclizations, the compound was the angular dihydrofuroquinoline (**8**). Oxidative cleavage of *N*-methylpreskimmianine (**1**) with osmium tetroxide–sodium periodate gave the aldehyde (**9**) in 82% yield. Its structure was indicated by its ^{1}H NMR spectrum [δ 3.65 (2H, *d*, CH_2), 3.76 (3H, *s*, NMe), 3.80 (3H, *s*, OMe), 9.65 (1H, *t*, CHO)] and by an IR absorption at 1720 cm^{-1}. Attempted cyclization of **9** with polyphosphoric acid following the method of Grundon *et al.* for the synthesis of isodictamnine [7], however, failed to give isoskimmianine (**10**) presumably because of inappropriate conditions of reaction. According to Grundon and co-workers [7] the cyclization reaction with polyphorphoric acid can give at least two products, depending on the reaction conditions.

1-Hydroxyrutaecarpine (**11**), present in small quantities, was poorly soluble in common organic solvents but it crystallized from a large quantity of MeOH to give a yellow powder, mp 316–318°. From analytical and MS data the molecular formula $C_{18}H_{13}N_3O_2$ was assigned. Its IR showed peaks at ν_{max} (KBr) 3340, 3275 and 1660 cm^{-1}, respectively, attributable to an OH group, an NH group and a tertiary amide function. The UV maxima (see Experimental) were also in agreement with a highly conjugated system. The high-

resolution ^{1}H NMR spectrum (100 MHz) of **11** was well resolved and showed two symmetrical triplets at 3.2 and 4.44 corresponding to $\geqslant$C–CH_2–CH_2–N$<$, a complex signal of six aromatic protons between δ 7.01 and 7.8, a broad singlet at δ 9.18 (exchangeable with D_2O) for an OH group and an indolic NH absorption at δ 11.50. Of particular significance in the spectrum was a one-proton doublet of doublets ($J_{4,3}$ = 8 Hz and $J_{4,2}$ = 2 Hz) at δ 8.0. Its down-field position indicated that it was H-4 deshielded by the *peri*-C-5 carbonyl function and its splitting pattern showed that it was coupled to H-3 and H-2. Comparison of these data with those published [10] for 1-hydroxyrutaecarpine (**11**) isolated from *Euxylophora paraenis*, also of the Rutaceae, showed their identity. This was confirmed by direct comparison (IR, TLC, mmp) with an authentic sample of 1-hydroxyrutaecarpine.

The second indolopyridoquinazoline alkaloïd (**12**), M^+ at *m/z* 301, mp > 340°, was also phenolic ($FeCl_3$) and exhibited UV absorptions at λ_{max} (CH_3CN) 230, 258, 294, 312, 363, 381 and 402 nm. Evidence for a double bond between C-7 and C-8 in **12** was obtained from its 100 MHz-FT ^{1}H NMR spectrum (DMSO-d_6) which lacked signals for the $\geqslant$C–CH_2–CH_2–N$<$ residue present in **11** and showed an AMX pattern at δ 7.85 and 8.55 ($J_{7,8}$ = 7.5 Hz). Because of the similarities between the UV spectrum of this alkaloïd and that of 1-hydroxyrutaecarpine (**11**) and their co-occurence, structure **12** was proposed for it. This structure was confirmed when DDQ dehydrogenation of **11** furnished a product indistinguishable from **12** on the basis of TLC, IR and mass spectral comparison.

Pairs of indolopyridoquinazolines like **11** and **12** differing only in their oxidation levels are rare in plants of the family Rutaceae. The only previous examples of such pairs so far known are euxylophoricine—A and B [11], euxylophoricine—D and E [12], euxylophorine—C and D [12] all obtained from *E. paraensis*.



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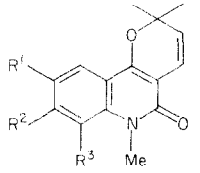
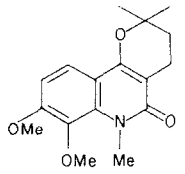


3 R^1 = H, R^2 = R^3 = OMe
4 R^1 = R^2 = OMe, R^3 = H



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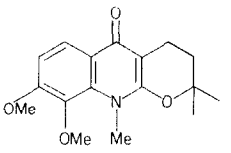

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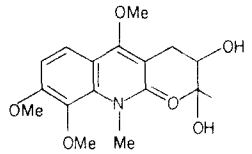

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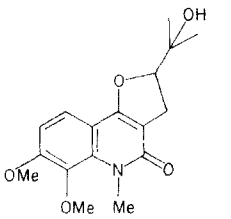

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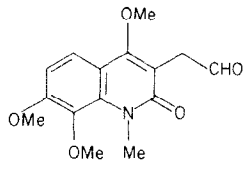

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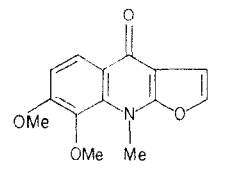

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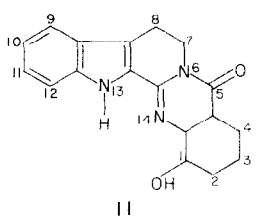

11

12 $\Delta^{7,8}$

EXPERIMENTAL

Powdered air-dried trunk bark of *Vepris louisii* G. Gilbert collected from Ngola near Lomié in the Eastern Province of Cameroon was successively extracted with hexane (24 hr), $CHCl_3$ (24 hr) and MeOH (12 hr). The concd hexane and $CHCl_3$ extracts were quantitatively similar (TLC) and were thus combined to give a dark green syrup (247 g). Part of this crude extract (62 g) was chromatographed on Si gel (Kieselgel 60; 70–230 mesh ASTM; 1.5 kg). Elution started with hexane and the polarity of the eluent was increased gradually. Compounds were eluted in the order given below and further purified on small columns or by prep. TLC.

Lupeol. Eluted with hexane–Et_2O (19:1). Colourless crystals from $CHCl_3$, mp 215–216° (lit. [13] 214–216°). *Acetate*, colourless needles, mp 215–216° (lit. [13]: 215.5–216.5). The isolate was identical in all respects (TLC, IR, ^{1}H NMR and MS) with an authentic sample, and a mmp determination showed no depression.

N-Methylpreskimmianine (**1**). Eluted with hexane–Et_2O (9:1). Colourless plates from hexane, mp 88–89°. IR: ν_{max}^{KBr} cm^{-1}: 1638 (2-quinolone > C=O), 1600, 1560, 1500 (aromaticity), 1460, 1432, 1380, 1360, 1325, 1290, 1260, 1195, 1110, 1075, 1050, 1010, 890, 855 and 810. UV: λ_{max}^{EtOH} nm (log ϵ): 226 (4.42), 236 (4.37), 253 (4.02), 261.5 (4.08), 300 (3.82), 323 (3.86) and 335 (3.75). EIMS (direct inlet), 70 eV, *m/z* (rel. int): 317 $[M]^+$ (30), 316 $[M-H]^+$ (98), 301 (98), 286 (19), 275 (32), 274 (100), 262 (69), 248 (75) and 178 (15). (Found: C, 68.24; H, 7.12; N, 4.39. $C_{18}H_{23}O_4N$ requires: C, 68.10; H, 7.31; N, 4.41%.)

Veprisine (**3**). Eluted with hexane–Et_2O (4:1). Pale yellow needles from hexane–C_6H_6, mp 89–90°. IR: ν_{max}^{KBr} cm^{-1}: 1646 (2-quinolone > C=O), 1630 (> C=C <), 1650, 1590, 1560, 1500 (aromaticity), 1460, 1370, 1335, 1295, 1270, 1260, 1190, 1160, 1130, 1080, 1070, 1010, 890, 870 and 820. UV: λ_{max}^{EtOH} nm (log ϵ): 236 (4.51), 263 (4.21) 273 (4.16), 334 (4.02), 349 (4.12) and 364 (3.93). MS: *m/z* 301 $[M]^+$ (40), 300 $[M-H]^+$ (95), 287 (86), 286 $[M-CH_3]^+$ (100), 256 (78), 242 (26), 228 (25) and 128 (29). (Found: C, 67.62; H, 6.48; N, 4.30. $C_{17}H_{19}O_4N$ requires: C, 67.76; H, 6.36; N, 4.65%.)

Methylation of preskimmianine (**2**) [4]. CH_3I (3 ml) and dry K_2CO_3 (1 g) were added to a soln of preskimmianine (2) (60 mg) in dry Me_2CO (100 ml). The reaction mixture was refluxed for 24 hr and then filtered to remove solid K_2CO_3. The solvent was evapd and the residue dissolved in $CHCl_3$ and washed with H_2O. Concn of the dried (Na_2SO_4) $CHCl_3$ layer and crystallization of the residue in hexane afforded **1** identical in all respects (IR, NMR, MS and TLC) with the natural product.

7,8 - *Dimethoxy* - 3,4,5,6 - *tetrahydro* - 2,2,6 - *trimethyl* - 5 - *oxo* - 2*H* - *pyrano* [3,2-*c*] *quinoline* (**5**) *and* 8,9 - *dimethoxy* - 3,4,5,10 - *tetrahydro* - 2,2,10 - *trimethyl* - 5 - *oxo* - 2*H* - *pyrano* [2,3-*b*] *quinoline* (**6**). A mixture of **1** (1 g) and conc. HCl was refluxed for 2 hr, cooled and excess 2 N NaOH added. Extraction with CH_2Cl_2 gave a semi-solid (980 mg) which showed two spots on a TLC plate. The crude mixture was chromatographed on Si gel. Elution with hexane–Et_2O (9:1) afforded the angular pyranoquinoline (**5**) (40 mg; 4%), colourless prisms from *n*-pentane, mp 76–78°. IR: ν_{max}^{KBr} cm^{-1}: 1640 (2-quinolone > C=O), 1610, 1590, 1500, 1460, 1385, 1315, 1262, 1165, 1110, 1055, 1010, and 985. UV: λ_{max}^{EtOH} nm (log ϵ_{max}): 325 (3.86), 313 (3.91), 297 (3.94), 248, (4.32), 233 (4.60), and 205 (4.11). $\lambda_{max}^{EtOH+HCl}$ (same as in λ_{max}^{EtOH}). ^1H NMR ($CDCl_3$): δ 1.50 (6H, *s*), 1.82 (2H, *t*, J = 7 Hz), 2.65 (2H, *t*, J = 7 Hz), 3.75 (3H, *s*, NMe); 3.95 (6H, *s*, 2 × OMe), 6.85 (1H, *d*, J = 10 Hz, H-6) and 7.7 (1H, *d*, J = 10 Hz, H-5). EIMS (direct inlet), 70 eV, *m/z* (rel. int): 303 (100), 288 (35), 261 (12), 260 (80), 249 (12), 248 (84), 247 (15), 232 (40) and 178 (37). (Found: C, 66.98; H, 7.20; N, 4.52. $C_{17}H_{21}O_4N$ requires: C, 67.31; H, 6.98; N, 4.62%.)

Elution of the column with hexane–Et_2O (1:4) furnished the linear pyranoquinoline (**6**) (860 mg; 86%), needles from EtOAc–pentane, mp 97–98°. IR ν_{max}^{KBr} cm^{-1}: 1610 (4-quinolone > C=O), 1610, 1545, 1505, 1445, 1296, 1080, 1045, 1015, 940 and 890. UV: λ_{max}^{EtOH} nm (log ϵ): 326 (4.10), 316 (4.13), 215 (4.66), 222 (4.28) and 204 (4.44). $\lambda_{max}^{EtOH+HCl}$ nm (log ϵ): 326 (4.19), 254 (4.73), 227 (4.44) and 204 (4.23). ^1H NMR (60 MHz; $CDCl_3$); δ 1.40 (6H, *s*, 2 × Me), 1.75 (2H, *t*, J = 7 Hz, $\underline{CH_2}$–CH_2–Ar), 2.65 (2H, *t*, J = 7 Hz, CH_2–$\underline{CH_2}$–Ar), 3.75 (3H, *s*, NMe), 3.80 (3H, *s*, OMe), 3.90 (3H, *s*, OMe), 6.95 (1H, *d*, J = 9 Hz, H-6) and 8.05 (1H, *d*, J = 9 Hz, H-5). EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 303 (78), 288 (12), 261 (14), 260 (87), 248 (100), 247 (22), 232 (30) and 178 (38). (Found: C, 67.42; H, 6.62; N, 4.40. $C_{17}H_{21}O_4N$ requires C, 67.31; H, 6.98; N, 4.62%.)

PdO *hydrogenation of veprisine* (**3**). **3** (100 mg) in MeOH (50 ml) was hydrogenated over PdO–C (70 mg). Filtration on Celite, evapn and recrystallization of the residue (93 mg) gave 7,8 - dimethoxy - 3,4,5,6 - tetrahydro - 2,2,6 - trimethyl - 5 - oxo - 2H - pyrano [3,2-c] quinoline (**5**) identical with **5** obtained from **1** by treatment with conc. HCl.

Conversion of **6** *to veprisine* (**3**). **6** (500 mg) in dry C_6H_6 (100 ml) was treated with DDQ (600 mg) in C_6H_6. The soln was refluxed for 2 hr, the solvent evapd and the residue chromatographed on Si gel. Elution with hexane–Et_2O (2:1) gave **3** indistinguishable from the natural sample TLC, IR, NMR and IR.

Peracid oxidation of N-*methylpreskimmianine* (**1**). **1** (250 mg) in $CHCl_3$ (50 ml) was stirred with 3-chloroperbenzoic acid (350 mg). After standing 2 hr at room temp., the soln was shaken successively with 2 N NaOH and H_2O, then dried and evapd to give crude 3 - (2,3 - dihydroxy - 3 - methylbutyl - 1 - methyl - 4,7,8 - trimethoxy - 2 - quinolone (**7**). Chromatographic purification (Si gel) yielded pure **7** (183 mg), prisms from EtOAc–pentane, mp 114–116°. IR: ν_{max}^{KBr} cm^{-1}: 3540 (non-bonded OH), 3270 (bonded OH), 1622 (chelated 2-quinolone > C=O), 1585, 1500, 1480, 1360, 1080, 1040 and 900. UV: λ_{max}^{EtOH} nm (log ϵ_{max}): 336 (3.99), 323 (4.08), 303 (4.04), 262 (4.26), 254 (4.24), 236 (4.58) and 227 (4.60). ^1H NMR (100 MHz, $CDCl_3$): δ 1.31 (6H, *s* 2 × Me), 2.67 (1H, *dd*, J = 13.5 Hz and 2 Hz, benzylic H), 3.05 (1H, *dd*, J = 13.5 Hz and 2 Hz, benzylic H), 3.58 (1H, *dt*, J = 2 Hz and 10 Hz), 3.81 (3H, *s*, Me), 3.92 (3H, *s*, OMe), 3.98 (6H, *s*, 2 × OMe), 5.18 (1H, *d*, J = 2 Hz, exchanged with D_2O, OH), 6.95 (1H, *d*, J = 9 Hz, H-6), and 7.55 (1H, *d*, J = 9 Hz, H-5). MS *m/z* (rel. int.); 351 $[M]^+$, 336 $[M-CH_3]^+$ (2), 333 $[M-H_2O]^+$ (4), 292 $[M-C_3H_2O]^+$ (100), 263 [M − side-chain]$^+$ (15), 262 (24), 248 (24) and 59 (4). (Found: C, 61.72; H, 7.03; N, 4.18. $C_{18}H_{25}O_6N$ requires C, 61.52; H, 7.17; N, 3.99%.)

The angular furoquinolone (**8**). **7** (100 mg) in dil. H_2SO_4 (25%; 20 ml) was heated at 80° for 2 hr. The soln was cooled and neutralized with 2 N NaOH. Extraction with $CHCl_3$ followed by evapn of the dried soln (Na_2SO_4) afforded a solid (90 mg). Crystallization in EtOAc–pentane afforded **8** as colourles needles, mp 131–132°. IR: ν_{max}^{KBr} cm^{-1}: 3440–3340 (OH), 1655 (2-quinolone > C=O), 1622, 1590, 1505, 1460, 1300, 1250, 1110, 1070, 1000, 765 and 730. UV: λ_{max}^{EtOH} nm (log ϵ_{max}): 330 (3.99), 316 (4.00), 304 (4.03), 252 (4.36), 234 (4.66) and 206 (4.20). ^1H NMR ($CDCl_3$): δ 1.25 (3H, *s*, Me), 1.35 (3H, *s*, Me), 2.60 (1H, *br s*, exchangeable with D_2O,OH), 3.12 (2H, *d*, J = 9 Hz), 3.78 (3H, *s*, NMe), 3.90 (3H, *s*, OCH_3), 3.95 (3H, *s*, OMe), 4.85 (1H, *t*, J = 9 Hz). 6.82 (1H, *d*, J = 9 Hz) and 7.48 (1H, *d*, J = 9 Hz), MS, *m/z* (rel. int.): 319 $[M]^+$ (90), 304 (50), 286 (60), 260 (100), 248 (18), 246 (25), 232 (28), 230 (18), 218 (14), 178 (32), 59 (82) and 43 (40). No analyses.

3 - *Formylmethyl* - 1 - *methyl* - 4 - 7,8 - *trimethoxy* - 2 - *quinolone* (**9**). **1** (100 mg) in dioxan–H_2O (3:1; 50 ml) was stirred at room temp. with OSO_4 (50 mg) and $NaIO_4$ added slowly. After 24 hr the reaction mixture was extracted with $CHCl_3$, washed with H_2O, dried (Na_2SO_4) and evapd to leave a dark residue which was filtered through a Si gel column. Elution with Et_2O afforded **9** which crystallized from $CHCl_3$–Et_2O as pale yellow prisms, mp 138–139°. IR ν_{max}^{KBr} cm^{-1}: 1720 (> C=O), 1640 (> C=O, 2-quinolone), 1600, 1500, 1460, 1365, 1325, 1290, 1120, 1081, 1062, 1008 and 790. UV λ_{max}^{EtOH} nm (log ϵ): 227 (4.32), 236 (4.32), 251 (4.2), 260 (4.04), 302 (3.78), 324 (3.89) and 336 (3.83). ^1H NMR ($CDCl_3$): 3.65 (2H, *d*, J = 2 Hz, $\underline{CH_2}$–CHO), 3.76 (3H, *s*, NCH_3), 3.80 (3H, *s*, OCH_3), 6.82 (1H, *d*, J = 9 Hz, H-6), 7.45 (1H, *d*, J = 9 Hz, H-5) and 9.65 (1H, *t*, J = 2 Hz, CH_2–$C\underline{H}$=O). MS, *m/z* (rel. int.): 263 $[M-CO]^+$ (80), 262 (23), 248 (100), 232 (19), 218 (17), 204 (14), 178 (28), 116 (17), 77 (26) and 51 (28). (Found: C, 61.75; H, 5.90; N, 4.49; $C_{15}H_{17}O_5N$ requires C, 61.85; H, 5.88; N, 4.81%.)

Isoskimmianine (**10**). The aldehyde (**9**) (40 mg) in polyphosphoric acid (15 g) was heated at 180–190° for 30 min then added to H_2O. The product was extracted with $CHCl_3$, the $CHCl_3$ soln dried (Na_2SO_4) and evapd to leave a residue (18 mg) which on TLC showed a tarry mixture which could not be resolved into any identifiable components.

1-*Hydroxyrutaecarpine* (**11**). Elution with hexane–Et_2O (2:3) gave a yellow solid (80 mg) which was very sparingly soluble in the usual organic solvents. On heating with MeOH, a fraction of the solid dissolved (23 mg) while most of it remained undissolved (50 mg). The soluble fraction was shown by TLC to be pure **11**, mp of yellow powder 316–318° IR ν_{max}^{KBr} cm^{-1}: 3340, 3275, 1660, 1630, 1607, 1570, 1533, 1500, 1440, 1394, 1322 and 720. UV λ_{max}^{MeOH} nm (log ϵ): 286 (3.78), 293 (3.83), 332 (4.34), 348 (4.45), 361 (4.53) and 379 (4.42). ^1H NMR: 3.20 (2H, *t*, J = 7 Hz, H_2-8), 4.44 (2H, *t*, J = 7 Hz, H_2-7), 7.01–7.8 (6H, *m*, aromatic protons), 8.0 (1H, *dd*, $J_{4,3}$ =

8 Hz, $J_{4,2}$ = 2 Hz, H-4), 9.18 (1H, *br s*, OH), 11.50 (1H, *br s*, NH); EIMS *m/z* (rel. int.): 303 $[M]^+$ (100), 302 (72), 169 (3.8) and 168 (9.4).

7,8-*Dehydro* - 1 - *hydroxyrutaecarpine* (**12**). The solid left after solubilization of 1-hydroxyrutaecarpine was shown by TLC to be homogeneous. Repeated washing with hot MeOH gave pure **12**, yellow powder, mp > 340°. IR ν_{max}^{KBr} cm^{-1}: 3360, 3270, 1690, 1670, 1640, 1610 (sh), 1580, 1550, 1490, 1380, 1330, 1245, 1145 and 720. ^1H NMR (DMSO-d_6): 7.2–7.8 (*m*, 6H, aromatic protons), 7.85 (1H, *d*, $J_{7,8}$ = 7.5 Hz, H-8), 8.18 (1H, *dd*, $J_{4,3}$ = 8 Hz, $J_{4,2}$ = 2 Hz, H-4), 8.55 (1H, *d*, $J_{8,7}$ = 7.5 Hz, H-7), 9.36 (1H, *br s*, OH-1), 12.36 (1H, *br s*, N–H). MS, *m/z* (rel. int.): 301 $[M^+]$ (100), 300 (4), 272 (4), 244 (10), 167 (7), 168 (46), 169 (7) and 140 (13). UV: λ_{max}^{MeCN} nm (log ϵ_{max}): 230 (4.70), 258 (4.69), 294 (4.44), 312 (4.30), 363 (4.44), 381 (4.64), 402 (4.68).

Conversion of 1-*hydroxyrutaecarpine into* **12**. 1-Hydroxyrutaecarpine (15 mg) in dry C_6H_6 (20 ml) was treated with DDQ (20 mg). The soln was refluxed for 2 hr and the solvent evapd *in vacuo* to leave a yellow residue. Co-TLC of the residue with natural **12** showed the compounds were identical. The IR spectrum of the residue was also superimposable with that of natural **12**.

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