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ISOQUINOLINE DERIVED ALKALOIDS FROM *BERBERIS CHITRIA**

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Key Word Index—*Berberis chitria*; Berberidaceae; aporphine; protoberberine; bisbenzylisoquinoline; *O*-methylcorydine-*N*-oxide.

Abstract—A new aporphine base characterized as *O*-methylcorydine-*N*-oxide together with berberine, palmatine, jatrorrhizine and oxyacanthine has been isolated from *Berberis chitria*.

In view of the reported spermatogenic activity [1] in the crude alkaloidal fraction of *B. chitria* and the exhibition of the CVS activity by its ethanol extract residue in a routine general screening programme [2], the phytochemical study of this hitherto uninvestigated plant seemed desirable. Accordingly, chromatographic separation of the crude base afforded a new aporphine alkaloid as an amorphous solid, $C_{21}H_{25}NO_5$, $[M]^+$ *m/z* 371 (FDMS); UV λ_{max}^{MeOH} nm: (log ε), 222 (4.6), 271 (4.18), and 302 (3.68). The ^1H NMR spectrum of the base revealed the presence of four methoxyl groups [δ3.76 (C-1, C-11), 3.90 (C-2), 3.95 (C-10)] and three aromatic protons at δ6.82 (H-3), 6.92 (H-8) and 6.94 (H-9). The substitution pattern at C-1, C-2, C-10 and C-11 was also inferred by the study of its mass spectrum in which after the expulsion of 16 mu from the molecular ion; the cracking pattern of the rest of the fragment corresponded to those of *O*-methylcorydine [3]. The fifth oxygen, as required by the molecular formula, was probably involved in *N*-oxide formation, an expedient considered justified due to the quaternary nature of the nitrogen (δ3.34, $[N-Me]^+$) and supported by a fragment ion at *m/z* 355 $[M-16]^+$ constituting the base peak in the mass spectrum. Final proof of the structure was obtained by the conversion of the base to *O*-methylcorydine [4] on treatment with ferrous sulphate and thus its identification as *O*-methylcorydine-*N*-oxide. Other bases isolated and characterized were berberine, palmatine, jatrorrizine and oxyacanthine.

The crude base mixture when administered at a dose level of 200 mg/kg in rats for 60 days failed to show the reported spermatogenic activity.

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EXPERIMENTAL

^1H NMR spectra were recorded at 90 and 80 MHz using TMS as internal standard. MS were recorded using a direct inlet system.

Isolation of constituents. Air-dried whole plant of *Berberis chitria* L. (5 kg) was percolated with 95% EtOH (5 × 10 l.) and the alcoholic residue fractionated into tertiary (1.1 g) and quaternary (40 g) bases. CC of the former on silica gel afforded oxyacanthine (40 mg). The quaternary alkaloidal mixture (10 g) was chromatographed on a neutral alumina column to yield a mixture of berberine and palmatine (4 g), which were separated and identified as their tetrahydro derivatives. Further elution of the column with 20% MeOH in $CHCl_3$ gave the *O*-methylcorydine-*N*-oxide (40 mg), **1**, $[\alpha]_D^{35}$ +193° (*c* 1; MeOH); IR ν_{max}^{KBr} cm^{-1}: 1605, 1440, 1420, 1240, 1112, 1060, 820; EIMS *m/z*: 371 $[M]^+$, 355, 340, 325, 310, 204; FDMS *m/z* (rel. int.): 371 $[M]^+$, 355 (100) Further elution of the column yielded jatrorrhizine (100 mg).

Conversion of **1** *into O-methylcorydine.* **1** (15 mg) in MeOH (1 ml) was heated with a soln of $FeSO_4$ (10%, 2 ml) at 80° for 30 min, cooled and extracted with $CHCl_3$. *O*-Methylcorydine was isolated as the hydrochloride salt, mp 260° (d) (MeOH–Et_2O).

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