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SPECTABILINE, A NEW DIHYDROFUROQUINOL-4-ONE ALKALOID FROM LEMONIA SPECTABILIS LINDL.

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Of the four alkaloids isolated from the petroleum ether extract of the leaves of Lemonia spectabilis Lindl. (Syn. Ravenia spectabilis Engl.) (Fam. Rutaceae), three have been identified as γ-fagarine[1] (major), atanine[2,3] [3-(3,3-dimethyl allyl)-4-methoxy-2-quinolone] and ravenine[3,4] [N-methyl-4-(3,3-dimethylallyloxy)-2-quinolone] on the basis of their spectral studies (UV, IR, NMR, MS[5]).

The fourth alkaloid, named spectabiline (yield 0.0045%), $C_{15}H_{17}O_2N$ (M^+ 243), m.p. 98-99° (hydrate) (heavy needles from petroleum ether-acetone mixture), $[\alpha]_D$ -5.9° (c 0.679 in $CHCl_3$), [R_f 0.46, silica gel G adsorbent, chloroform-methanol (97:3) developer], picrate, m.p. 198°d; turned out to be a new one and we propose structure I for it on the basis of evidences presented below.

Spectabiline exhibited UV spectrum [λ_{max} (EtOH) 230 nm (log ϵ, 4.30), 249 sh (4.15), 307.5 (4.04) and 317 (4.02); λ_{min} 265 (3.30) and 314 (3.98)] typical of 2-alkoxy-4-quinolone[6] chromophore. The spectrum was unchanged in alkali medium indicating absence of phenolic -OH (negative $FeCl_3$). The absence of any maximum in the region 265-295 nm as well as the pronounced hypsochromic shift of the long wave-length bands in acid medium [λ_{max} (EtOH-HCl) 235 nm (log ϵ, 4.41), 295 (4.07) and 302 (4.06)] further corroborates[6] the 4-quinolone (and not 2-quinolone) structure for this alkaloid.

The IR bands (KBr) at 1615, 1570, 1535 and 1500 cm^{-1} fit the criteria for a 2-alkoxy-4-quinolone moiety[6]. The broad band above 3000 cm^{-1} (ν_{max} 3450 cm^{-1}), although the molecule has no acetylatable nitrogen or oxygen, is ascribed to the unusual rapacity of spectabiline for water of crystallisation - a phenomenon quite common for N-alkyl-furoquinol-4-one[7] alkaloids.

The PMR spectrum ($CDCl_3$, 60 MHz) revealed the details of its structure in such a way as to permit its formulation as I. The spectrum contains evidence of a secondary methyl group (3H, d, 1.35 ppm; 1H, q, 3.38 ppm; J = 7 Hz), a quaternary gem-dimethyl attached to an oxygen-bearing

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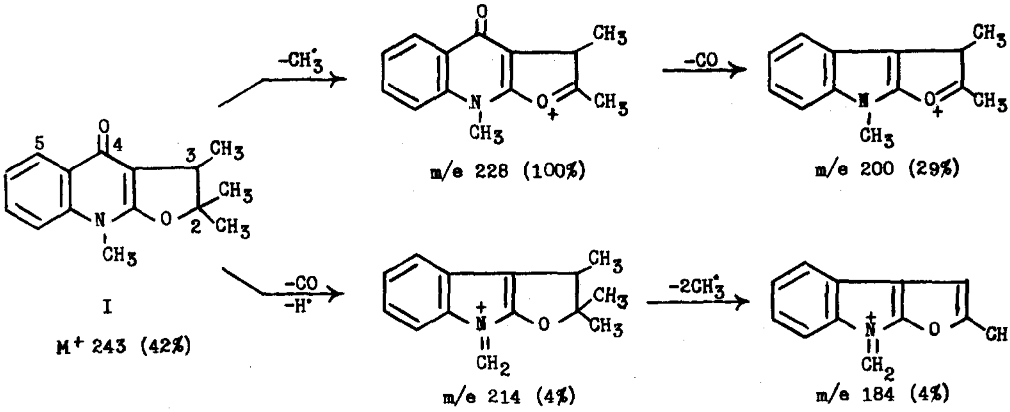
carbon (3H each, s, 1.47 and 1.49 ppm), an N-methyl group (3H, s, 3.65 ppm) and four adjacent aromatic protons (3H, m, 7.2-7.5 ppm, H-6, H-7 and H-8; 1H, q, 8.47 ppm, H-5, $J_{\underline{ortho}} \sim 8.5$ Hz, $J_{\underline{meta}} \sim 2$ Hz, $J_{\underline{para}} \sim 0$ Hz). The far downfield position of the H-5 signal (strongly deshielded by the *peri*-carbonyl) again confirms the presence of 4-quinolone moiety[8] rather than 4-alkoxy-2-quinolone structure in which case H-5 appears around 8 ppm (cf. atanine and ravenine). A sharp singlet appearing at 2.35 ppm (integrating for 1.3 protons for the sample dried at 55° for 8 hr. under 1 mm pressure over P_2O_5), readily exchangeable with D_2O, is evidently due to hydroxyl protons. This is consistent with the earlier finding that stable hydrate formation occurred with N-alkyl furoquinol-4-one derivatives[9] and unless the sample was very scrupulously dried (*e.g.* at 90° under 0.1 mm pressure for 72 hr. over P_2O_5 in case of acrophylline[7]), a singlet appeared in 2-4 ppm region, disappearing on deuteration[9].



I

M+ 243 (42%)

Scheme I. Fragmentation of spectabiline

The mass spectral fragmentation pattern (Scheme I) lends further support to the suggested structure I for spectabiline. Further work on this alkaloid is in progress.

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