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A NEW 4,5 - DIOXOAPORPHINE AND OTHER CONSTITUENTS OF ARISTOLOCHIA INDICA[1,2]

Basudeb Achari, Sarmistha Chakrabarty, Soumitra Bandyopadhyay and
Satyesh C.Pakrashi*
Indian Institute of Chemical Biology, Calcutta-700 032, India

Abstract — A new 4,5-dioxoaporphine, deduced to be 2-hydroxy-1-methoxy-4H-dibenzo[de, g]quinoline-4,5(6H)-dione (4a) from spectroscopic evidences, cepharadione A (4c) , aristololactam AII (2b) and β-sitosterol-β-D-glucoside have been encountered in the roots of Aristolochia indica Linn.

Earlier communications from this laboratory described the isolation of some new phenanthrene derivatives[3] related to aristolochic acid (1) and aristololactam (2a) besides a novel type[4] of sesquiterpene (3) from the roots of Aristolochia indica Linn. (Aristolochiaceae), shown to have encouraging antifertility activity[5]. We now report the isolation and characterisation of three more highly fluorescent lactams along with β-sitosterol-β-D-glucoside from the same source. All of them were obtained by column chromatography of the alcoholic extract depleted of the acidic constituents.

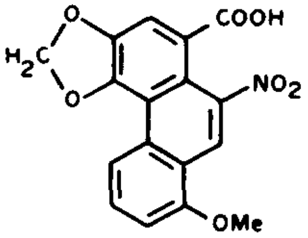
One of them, a new compound crystallised in red needles ($CHCl_3$-MeOH), mp 310-312°, could be assigned the molecular composition $C_{17}H_{11}NO_4$ from high resolution mass spectroscopy (Found and calcd. mass 293.0686). The spectrum was characterized by a direct loss of CO from the molecular ion (the base peak), not observed in any of the phenanthrene derivatives isolated so far[3] from this plant, leading to a prominent peak at m/z 265(27%). Subsequent methyl loss accounted for the other significant peak at m/z 250(51%).

The uv spectrum of the compound in ethanol [λ_{max}(log ε) : 246(4.70), 292sh (4.14), 305(4.26), 318(4.28),459(4.23) nm] was reminescent of that of aristololactam (2a), a co-occurring constituent, except that the peaks suffered considerable bathochromic shifts. Further shift towards the longer wave length region was observed on addition of alkali [λ_{max}(log ϵ) 241(4.71), 256(4.67), 305sh (4.10),321(4.21),331(4.25),510(4.30) nm]. The compound was, therefore, concluded to be a phenanthroid lactam with at least one phenolic group. The presence of an additional carbonyl group became evident from the ir spectrum (nujol) which displayed peaks at 1690 and 1665 cm^{-1} besides a broad peak around 3300 cm^{-1} for OH/NH, and other important bands at 1615, 1585, 1560, 1410, 1300, 1280, 1020, 955, 880 and 740 cm^{-1}.

The above evidences, particularly the facile loss of CO from the molecular ion in the mass spectrum, led to the structures 4a or 4b, supported by nmr evidences.

The ^{1}H nmr spectrum (270 MHz in DMSO-d_6), conspicuous by the absence of any signal for methylenedioxy group characteristic of all the other phananthrene derivatives isolated so far from this plant, contained two downfield exchangeable signals between δ 12-13, corroborating the presence of a NH and a phenolic OH. An aromatic methoxy group also became evident from a signal at δ 4.06. Further, multiplets at δ 9.46 and 7.93 could be assigned to H-11 and H-8 and singlets at δ 8.10 and 7.50 to H-3 and H-7, respectively. A two-proton multiplet at around δ 7.66 was similarly ascribed to H-9 and H-10. Both the structures are also in accord with biogenetic considerations, since aporphine bases are known to be the precursors of aristolochic acids. However, 4a appeared to be the structure of choice since the uv spectrum of the compound remained unaffected on addition of NaOAc, not compatible with structure 4b having the phenolic group para to the carbonyl. The compound was thus concluded to be 2-hydroxy-1-methoxy-4H-dibenzo[de,g]quinoline-4,5(6H)-dione(4a), a 4,5-dioxoaporphine hitherto not encountered in nature. Although this basic skeleton has been isolated recently from Menispermaceae[6,7], Papaveraceae[8] and Piperaceae[9], this is its first reported occurrence in Aristolochiaceae[10]. The co-occurrence of aristolochic acids, aristololactams and 4,5-dioxoaporphines, not reported earlier, is of considerable biogenetic significance (cf.ref.11).

The other two lactams proved to be known compounds, namely, cepharadione A(4c)[7,9] and aristololactam AII(2b)[12]. Their uv, ir, ^{1}H nmr and mass spectroscopic data were identical to those described in the literature. The identities were further confirmed by direct comparison with authentic specimen. Cepharadione A has not so far been reported from the family Aristolochiaceae, while for aristololactam AII this is only the second source in the genus Aristolochia.



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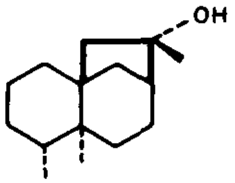

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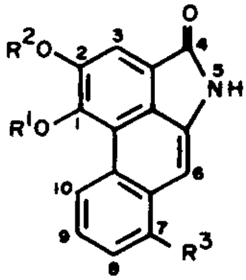
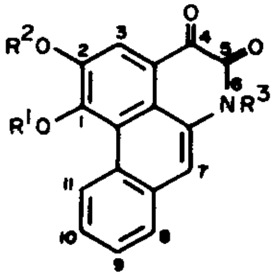


2a. $R^1+R^2=CH_2$, $R^3=OMe$
b. $R^1=Me$, $R^2=R^3=H$



4a. $R^1=Me$, $R^2=R^3=H$
b. $R^1=R^3=H$, $R^2=Me$
c. $R^1+R^2=CH_2$, $R^3=Me$

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