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FOUR NEW FLUORESCENT COMPONENTS ISOLATED FROM THE CALLUS TISSUE OF STEPHANIA CEPHARANTHA

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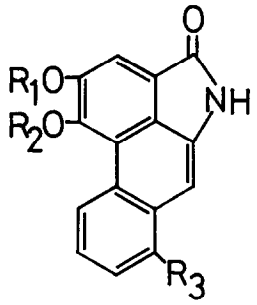
In the previous paper of this series, we reported that phytosterols of 4-en-3-one and 4-en-3,6-dione types have been isolated from the callus tissue of Stephania cepharantha Y. Hayata (Menispermaceae).[1] The present paper deals with the isolation of four new fluorescent components, which are related to aristololactam(V), from the callus tissue of S. cepharantha, named as cepharanone A, B and cepharadione A, B. Two biscoclaurine type alkaloids were also isolated from the callus tissue of the same plant.[2]

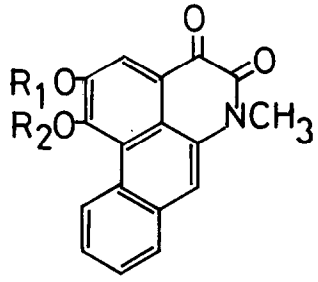
From the neutral fraction of the MeOH extract of the callus, four intense fluorescent compounds were isolated and the physical data of them are illustlated in Table I.

Table I

	formular	mp (°C)	crystal form (solvent)	fluorescence
I	$C_{16}H_9NO_3$	308-310	pale yellow amorphous (DMF)	blue
II	$C_{17}H_{13}NO_3$	264-265	pale yellow needles (Me_2CO)	blue
III	$C_{18}H_{11}NO_4$	350<	orange needles (DMF)	bright orange
IV	$C_{19}H_{15}NO_4$	267-268	orange needles (EtOH)	bright orange

Cepharanone A (I), IRν_{max}^{KBr}cm^{-1}; 3150(NH), 1706, 1690(CO). UVλ_{max}^{EtOH}nm(logε); 225(4.45), 232(4.49), 265(4.46), 277(4.53), 288(4.51), 328(4.06), 341(4.04), 376 (3.93), 393(3.93). Mass spectrum m/e(%); 263(100), 235(6.5), 207(5.8), 179(11.2) , 177(17.4). The NMR spectrum(DMSO,δ,ppm) of I showed a signal of methylene-dioxy group at 6.45(2H,s), two singlets of uncoupling aromatic protons at 7.10 and 7.60, coupling aromatic protons at 7.5-7.7(2H,m), 7.9(1H,m) and 8.5(1H,m), and NH signal at 10.75(broad s). On the basis of these data, I was assumed to be a lactam of aristolochic acid II, and was identified with the authentic sample derived from aristolochic acid II by Zn-AcOH reduction, by direct comparison of the mixed mp, IR, UV, Mass and NMR spectrum.





(I) $R_1+R_2 = CH_2$, $R_3=H$ (III) $R_1+R_2=CH_2$

(II) $R_1=R_2=CH_3$, $R_3=H$ (IV) $R_1=R_2=CH_3$

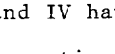
(V) $R_1+R_2=CH_2$; $R_3=OCH_3$

Cepharanone B (II) was also related compound of I on the basis of the following data. IRν_{max}^{KBr}cm^{-1}; 3150(NH), 1712(CO). UVλ_{max}^{EtOH}nm(logε); 232(4.43), 263(4.43), 276(4.48), 287(4.48), 319(4.00), 396(3.96). NMR spectrum(DMSO,δ,ppm) showed the singlet of two -OMe at 4.05(6H,s) instead of methylenedioxy group of I, and the aromatic proton of I shifted to downfield from 8.5 to 9.12. Mass fragmrnt pattern showed the characteristic peak of two OMe degradation, m/e 264 (M^+-Me), 236(M^+-Me-CO), 221(M^+-C_2H_3O-Me), 209(M^+-C_2H_3O-Me-CO). In conclusion, II was decided as 1,2-dimethoxy-4-oxo-Dibenzo(cd,f) indol.

Cepharadione B (IV), IRν_{max}^{KBr}cm^{-1}; 1667, 1650(CO). UVλ_{max}^{EtOH}nm(logε); 213(4.57) , 244(4.61), 273(4.20,sh), 303(4.26), 315(4.29), 440(4.23). NMR($CDCl_3$,δ,ppm); 3.64(3H,s,-NMe), 4.00(3H,s,-OMe), 4.03,(3H,s,-OMe), 7.22(1H,s,aromatic proton),

7.5-7.8(3H,m.aromatic protons), 7.98(1H,s,aromatic proton), 9.37(1H,m,aromatic proton). Mass m/e(%); 321 M^+(100), 293(84.1), 278(21.2), 263(8.3), 250(43.2), 235(28.8), 207(10.6), 179(40.9). It was suggested from these data that the structure of IV was similar to that of II. But NH signal was not observed, instead, a singlet of methyl group was noticed at 3.64 ppm(NMe). UV spectrum of IV showed the bathochromic shift comparing with II. The Mass fragment of m/e 293 was obtained by splitting CO from 321(M^+). The pattern of the fragments below 293 of IV showed also the similality to II. The presence of conjugated carbonyl group was estimated from IR, UV and Mass. Consequently, IV was suggested as the compound having conjugated carbonyl group in addition to the structure of II. So, the structure IV was suggested as 1,2-dimethoxy-4,5-dioxo-6-methyl-6a,7-dehydroaporphine.

Cepharadione A (III) was supposed to be the methylenedioxy type compound of IV, as the relationship between I and II, from the following data. IR$\nu_{max}^{KBr}cm^{-1}$; 1675, 1650(CO). UVλ_{max}^{EtOH}nm(logε); 219(4.59), 238(4.61), 265(4.21,sh), 279(4.20), 290(4.21), 303(4.24), 315(4.28), 439(4.26). NMR($CDCl_3$,δ,ppm); 3.52(3H,s,NMe), 6.20(2H,s,OCH_2O). Mass m/e(%); 305 M^+(87.9), 277(100), 263(9.9), 260(13.2), 248(11.0), 219(9.9), 190(14.3), 163(34.1), 150(15.4), 138(27.5).

The presence of these compounds were also observed in the intact plant but trace. III and IV having a unique system () in the structure are assumed to be the biogenetical intermediate of aristololactam type compounds, and this raises interesting biosynthetic question which formed the subject of further investigations.

The aristololactam group was known only in Aristolochiaceae together with the aristolochic acid group.[3,4] Hutchinson reported that Aristolochiaceae was the most closely related Family to Menispermaceae from the similarity of the stem structure.[5] These facts are very interesting problems from the chemotaxonomical point of view.

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