

Application of 2D NMR Spectroscopy in Structural Elucidation of some Phenanthrene Derivatives from Indian Orchidaceae Plants

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The structures of the phenanthrene derivatives confusarin (2,7-dihydroxy-3,4,8-trimethoxyphenanthrene) and confusarinidin (2,6-dihydroxy-3,4,7,8-tetramethoxyphenanthrene), bulbophyllanthrin (3,5-dihydroxy-2,4-dimethoxyphenanthrene), gymnopusin (2,7-dihydroxy-3,4,9-trimethoxyphenanthrene) and cirrhopetalanthrin (2,2',7,7'-tetrahydroxy-4,4'-dimethoxy-1,1'-biphenanthryl) [isolated from the Indian Orchidaceae plants *Eria confusa*, *Bulbophyllum leopardium*, *Bulbophyllum gymnopus* and *Cirrhopetalum maculosum* respectively] deduced mainly from ^1H and ^{13}C nmr spectral evidence have been established unequivocally from both homonuclear (^1H - ^1H) and heteronuclear (^1H - ^{13}C) 2D nmr correlation studies.

Two-dimensional nmr spectroscopy^{1,2} has turned up to be one of the most powerful physical tools since 1980s for the structural elucidation of organic molecules. During the last one decade the structures of a large number of complex natural products were established unambiguously by their 2D nmr spectral data, which were, otherwise, extremely difficult to be settled by the more conventional spectral evidence. As part of our general programme of research on the chemical constituents of Indian Orchidaceae plants we have chemically investigated more than six dozens of Himalayan orchids which afforded a large number of compounds comprising mostly a wide range of stilbenoids³⁻⁵, besides several triterpenoids⁶ and steroids⁷ of biogenetic importance. In this communication we present the results of the 2D nmr spectral analysis of five representative phenanthrene derivatives, viz. confusarin⁸ (1a) and confusarinidin⁸ (1c), bulbophyllanthrin⁹ (2a), gymnopusin^{10,11} (1e), and cirrhopetalanthrin¹² (3a) [isolated from the orchids *Eria confusa*, *Bulbophyllum leopardium*, *Bulbophyllum gymnopus* and *Cirrhopetalum maculosum*

respectively] to illustrate the power and utility of this physical method for the structural elucidation of these compounds. The structures of these compounds deduced mainly from conventional spectral evidence, viz. ^1H nmr (Table 1) and ^{13}C nmr (Table 2) have since been established unequivocally by extensive homonuclear (HOMCOR or COSY) [^1H - ^1H] and heteronuclear (HETCOR or XHCORR) [^1H - ^{13}C] 2D nmr correlation analysis as discussed below.

The structures of confusarin (1a) and confusarinidin (1c) are in good agreement with the ^1H nmr spectral data of the compounds and their diacetyl derivatives 1b and 1d and are further supported by the ^{13}C nmr spectral data of 1a, 1b, and 1c. Yet these data seemed inadequate for establishing the relative positions of the oxygen functions and the assignments of some of the ^1H and ^{13}C chemical shifts unambiguously, which were finally confirmed by 2D nmr spectral analysis of the compounds. The homonuclear (^1H - ^1H) correlation experiment (COSY) with confusarin confirmed the couplings between H-5 (δ 9.12) and H-6 (δ 7.22) and H-9 (δ 7.79) and H-10 (δ 7.51), but showed no 5-bond ^1H - ^1H coupling between any of the methoxyl groups with an *o*-proton. This confirmed that none of the methoxyl groups in confusarin had an *o*-hydrogen atom — a conclusion which was also in agreement with the relatively downfield shifts of all the methoxyl carbon resonances of confusarin. The COSY spectrum of confusarinidin (1c), (Fig. 1), on the other hand, showed, besides the expected coupling between H-9 (δ 7.89) and H-10 (δ 7.42), a number of weak peaks representing long range ^1H - ^1H couplings which are normally not observed in simple aromatic compounds. These weak peaks corresponded to a 5-bond coupling between H-5 (δ 8.83) and H-9 (δ 7.89), a 4-bond coupling between H-1 (δ 7.14) and H-10 (δ 7.42), a 5-bond coupling between H-1 and H-9 and a 6-bond coupling between

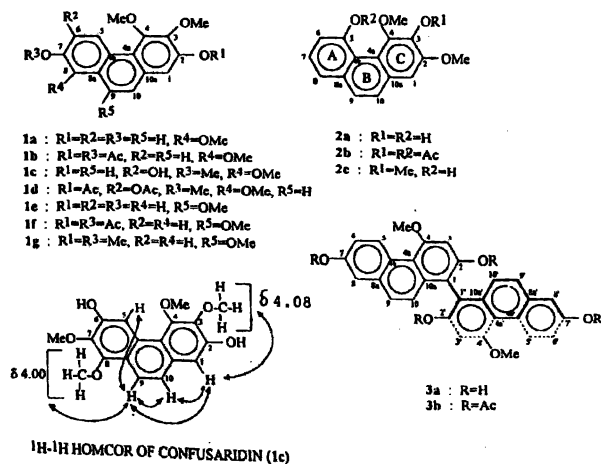


TABLE 1—¹H NMR SPECTRAL DATA (δ, J in Hz) OF COMPOUNDS 1-3

Compd.	H-1	H-3	H-5	H-6	H-7	H-8	H-9, H-10	OH/OAc/OMe
1a	7.11(s)	—	9.12 (d, J 10)	7.22 (d, J 10)	—	—	7.79, 7.51 (each d, J 10)	5.90 (2H, s, 2 × OH), 3.89 (6H, s, 2 × OMe), 4.03 (3H, s, OMe)
1b	7.40(s)	—	9.37 (d, J 9.2)	7.36 (d, J 9.2)	—	—	8.05, 7.65 (each d, J 9.1)	4.01, 3.99, 3.98 (each 3H, s, 3 × OMe), 2.43, 2.41 (each 3H, s, 2 × OAc)
1c	7.14	—	8.83(s)	—	—	—	7.89, 7.42 (each d, J 9)	5.97, 6.00 (each 1H, s, 2 × OH), 3.97, 4.00 (each 3H, s, 2 × OMe), 4.08 (6H, s, 2 × OMe)
1d	7.40	—	9.10(s)	—	—	—	8.04, 7.62 (each d, J 10)	4.04, 4.02, 4.01, 3.97 (each 3H, s, 4 × OMe), 2.43, 2.41 (each 3H, s, 2 × OAc)
1e	7.08(s)	—	9.33 (d, J 9.3)	7.21 (dd, J ₁ 9.3, J ₂ 2.8)	—	7.69 (d, J 2.8)	— 6.94(s)	3.96 (6H, s, 2 × OMe), 4.02 (3H, s, OMe)
1f	7.26(s)	—	9.58 (d, J 9.3)	7.41 (dd, J ₁ 9.3, J ₂ 2.8)	—	8.07 (d, J 2.8)	— 6.86(s)	4.0 (6H, s, 2 × OMe), 4.02 (3H, s, OMe), 2.33, 2.40 (each 3H, s, 2 × OAc)
1g	6.89(s)	—	9.39 (d, J 9.4)	7.25 (dd, J ₁ 9.4, J ₂ 2.9)	—	7.72 (d, J 2.9)	— 6.99(s)	3.98 (6H, s, 2 × OMe), 4.06, 3.99, 3.96 (each 3H, s, 3 × OMe)
2a	7.15(s)	—	—	7.26 (dd, J ₁ 8, J ₂ 2)	7.51 (app.t J 8)	7.42 (dd, J ₁ 8, J ₂ 2)	7.50, 7.57 (each d, J 8)	5.99, 10.30 (each 1H, s, 2 × OH), 3.85, 4.07 (each 3H, s, 2 × OMe)
2b	7.13(s)	—	—	7.72 (dd, J ₁ 8, J ₂ 2)	7.65 (app.t J 8)	7.42 (dd, J ₁ 8, J ₂ 2)	7.56, 7.67 (each d, J 8)	4.01, 3.39 (each 3H, s, 2 × OMe), 2.45, 2.37 (each 3H, s, 2 × OAc)
2c	7.19(s)	—	—	7.28 (dd, J ₁ 8.8, J ₂ 1.7)	7.53(t)	7.46 (dd, J ₁ 8.8, J ₂ 1.7)	7.64, 7.52 (each d, J 8)	3.87, 4.05, 4.12 (each 3H, s, 3 × OMe), 10.50 (1H, s, OH)
2d	7.03(s)	—	—	7.08 (dd, J ₁ 8.8, J ₂ 1.7)	7.48(t)	7.42 (dd, J ₁ 8.8, J ₂ 1.7)	7.51, 7.53 (each d, J 8)	3.76, 4.03 (each 3H, s, 2 × OMe), 4.02 (6H, s, 2 × OMe)
3b	—	7.14(s)	9.77 (d, J 9.4)	7.42 (dd, J ₁ 9.4, J ₂ 2.4)	—	7.56 (d, J 2.4)	7.49, 7.16 (each d, J 9.1)	4.25 (6H, s, 2 × OMe), 2.40, 1.83 (each 6H, s, 4 × OAc)

H-1 and the protons of the methoxyl group at C-3 (δ 4.08). Such 6-bond coupling between H-1 and OMe at C-3 is perhaps strong enough to be observed due to OH at C-2. Another extremely weak 6-bond coupling between H-9 and protons of the methoxyl group at C-8 (δ 4.00) was also discernible. But a more significant observation was the absence of a coupling between H-5 with the protons of any of the OMe groups. This may be attributed to the presence of an OH at C-6 and OMe at C-7 and C-8. These ¹H-¹H correlations in **1c** are shown in its structural diagram.

The 1-bond heteronuclear (¹H-¹³C) correlation experi-

ments with both confusarin (**1a**) and confusarinidin (**1c**) using *J*_{CH} parameter set to 160 Hz confirmed the chemical shifts of the protonated carbon atoms from the readily identifiable protons and vice versa in both the compounds. But these experiments failed to assign specifically the C-9 and C-10 carbon resonances of the compounds, since the assignments of the H-9 and H-10 resonances of the compounds were still arbitrary. The long-range heteronuclear (¹H-¹³C) correlation plots of both **1a** (Fig. 2) and **1c** (Fig. 3) using *J*_{CH} parameter set to 7 Hz not only enabled to identify the C-9, C-10 and H-9 and H-10 resonances but also provided

TABLE 2—¹³C NMR SPECTRAL DATA (δ_c) OF 1a, 1b, 1c, 1e, 1f, 1g, 2a, 2c AND 3b

Carbon atom	1a*	1b*	1c*	1e**	1f*	1g*	2a*	2c*	3b*
C-1(C-1')	107 61	117 23	107 28	108 41	115 75	104 18	106 00	107 87	119 18
C-2(C-2')	147 12	145 09	147 73	149 68	143 43	151 80 ^a	146 90	152 35 ^c	147 84
C-3(C-3')	140 40	143 49	139 86	140 52	142 86	140 99	138 90	142 26	104 07
C-4(C-4')	150 16	152 69	150 56	155 44	152 48	151 97 ^a	140 71	154 20	159 18
C-4a(C-4a')	118 45	123 21	117 54	114 75	118 85	114 92	117 11	117 27	117 53
C-4b(C-4b')	124 27	129 56	126 65	125 04	128 49	125 21	117 69	120 52	128 19
C-5(C-5')	123 38	123 95	106 25	128 48	128 66	128 22	154 24	152 16 ^c	130 18
C-6(C-6')	115 56	122 06	147 56	117 42	121 36	117 34	115 74	116 27	120 82
C-7(C-7')	144 92	140 74	137 50	151 78	148 85	157 25	127 43	130 51	148 48
C-8(C-8')	140 40	146 84	146 66	106 29	114 03	102 47 ^b	120 32	119 51	119 46
C-8a(C-8a')	125 73	128 41	120 92	128 30	128 12	127 42	134 53	134 36	133 50
C-9(C-9')	118 83	120 53	119 36	153 07	152 87	152 82 ^a	126 85	127 4 ^d	128 50
C-10(C-10')	126 83	127 36	123 78	102 78	102 52	102 51 ^b	126 14	128 25 ^d	125 65
C-10a(C-10a')	128 74	128 97	130 14	130 56	130 21	129 59	127 34	126 65	134 39
OMe	60 20	60 20	59 31	59 64	60 01,	60 19,	62 28	62 94,	56 09
	62 08	61 20	60 55	60 84	61 13	61 26	(OMe at	61 98	
	61 20	62 08	60 71	(OMe at	(OMe at	(OMe at	C-4),	(OMe at	
			60 72	C-3,	C-3,	C-3,	56 27	C-3,	
				C-4),	C-4),	C-4),	(OMe at	C-4),	
				55 39	55 46	55 29,	C-2)	56 0	
				(OMe at	(OMe at	55 40,		(OMe at	
				C-9)	C-9)	55 78		C-2)	
						(OMe at			
						C-2, C-7,			
						C-9)			
OAc	—	169 29	—	169 19	—	—	—	—	169 31
		20 88		169 57					169 68
		21 07		20 75					20 79
				21 19					21 36

*Spectra were run in CDCl₃ and the chemical shifts were measured with δ_{TMS} = δ_{CDCl₃} + 76.9 ppm**Spectrum was run in acetone-d₆ and the chemical shifts were measured with δ_{TMS} = δ_{acetone-d₆} + 29.6 ppm^a Values are interchangeable in each column

convincing evidence for the placement of the oxygen functions in the compounds. Thus, H-1 (δ 7.11) of 1a showed 3-bond correlations with the protonated carbon at δ_c 126.83 and the two nonprotonated carbons at δ_c 118.45 and 140.4. So, while δ_c 118.45 and 140.40 should be assigned to its C-4a and C-3 respectively, the signal at δ_c 126.83 corresponded to its C-10. Since the carbon at δ_c 126.83 showed 1-bond correlation with the proton at δ 7.51, the latter must correspond to H-10. This was further supported by the fact that the above proton (δ 7.51) exhibited 3-bond correlations with C-1 (δ_c 107.61), C-4a (118.45) and also with the carbon atom at δ_c 125.73 which should then be assigned to C-8a. The signal at δ 7.79 of 1a may then be assigned to its H-9 which exhibited 3-bond correlations with the carbons resonating at δ_c 124.27 (C-4b) and 128.74 (C-10a). H-9 of

1a, however, did not show any 3-bond correlation with its C-8 (δ_c 140.40). As in the case of 1a, H-1 (δ 7.14) of 1c also showed 3-bond correlations with the protonated carbon at δ_c 123.78 and two nonprotonated carbons at δ_c 117.54 and 139.86, which should therefore be assigned to C-10, C-4a and C-3 respectively. 1-Bond correlation of the carbon at δ_c 123.78 with the proton at δ 7.42 confirmed that the signal at δ 7.42 should be assigned to H-10 of 1c. This was further corroborated by the fact that the signal at δ 7.42 (H-10) also showed weak 3-bond correlations with C-1 (δ_c 107.28) and C-8a (δ_c 120.92). H-10 of 1c, however, did not exhibit the expected 3-bond correlation with its C-4a as in 1a. The remaining doublet proton signal at δ 7.89 of 1c must then be assigned to its H-9 which, in turn, exhibited 3-bond correlation with the carbon at δ_c 130.14

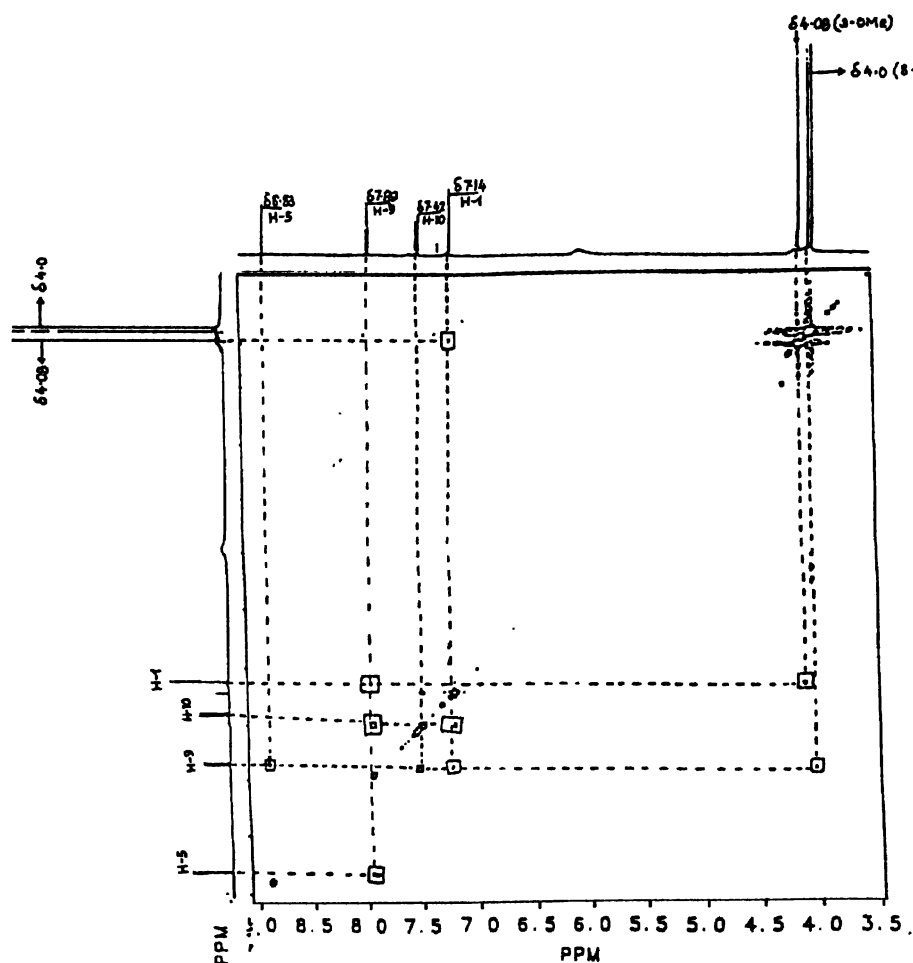
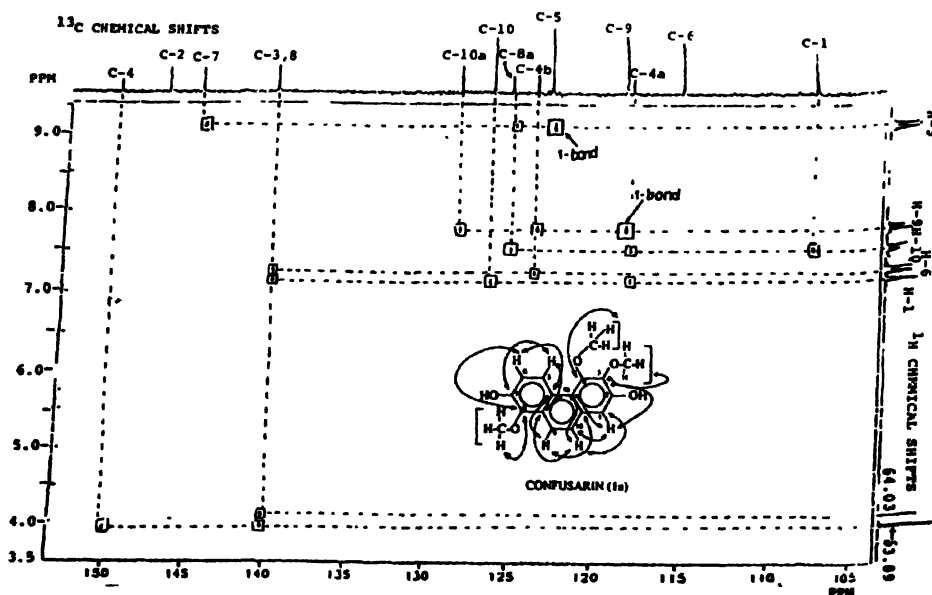
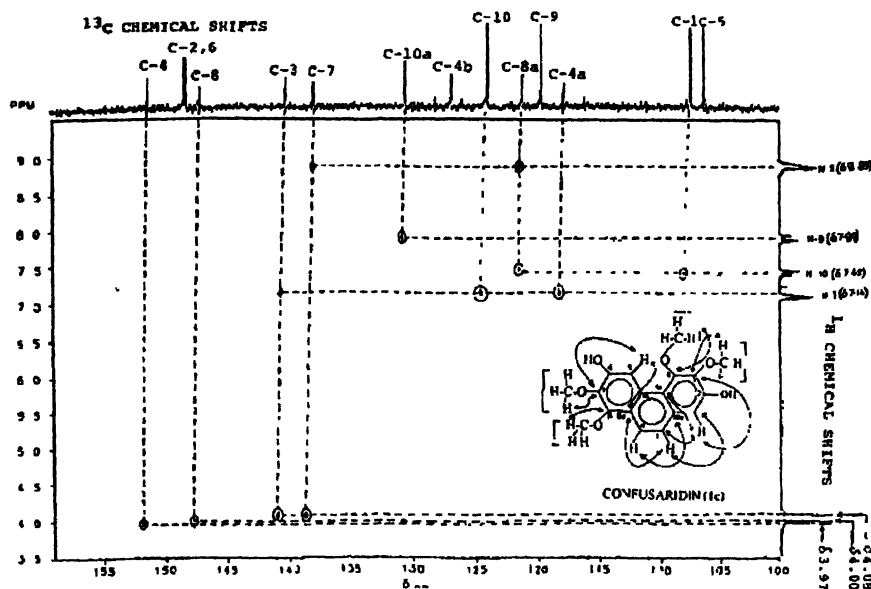


Fig. 1. HOMCOR contour plot of confusaridin (1c).

which could be conceived to correspond to its C-10a. H-9 of 1c, however, showed no 3-bond correlations with its C-8 and C-4b. 3-Bond correlations of H-5 (δ 9.12) of 1a were also observed with the carbon at δ_c 125.73 (C-8a) and also with that at δ_c 144.92 which should then correspond to its C-7 bearing one of the hydroxyl groups. Similar 3-bond correlations of H-5 (δ 8.83) of 1c with the carbons at δ_c 120.92 (C-8a) and 137.50 were discernible. The latter signal (δ_c 137.50) of 1c must then be assigned to its C-7 bearing one of its methoxyl groups. The doublet proton at δ 7.22 of 1a already assigned to its H-6 from COSY spectrum showed 3-bond correlations with the carbons at δ_c 124.27 (already assigned to C-4b) and 140.40. The latter signal should then correspond to C-8 of 1a. 3-Bond correlations of the methoxyl protons of 1a at δ 4.03 with carbon at δ_c 140.40 and those at δ 3.89 with δ_c 140.40 and 150.16 confirmed the chemical shifts of its methoxyl protons. Similar 3-bond correlations of the methoxyl protons of 1c at

δ 3.97 (3H), 4.00 (3H), and 4.08 (6H) with the carbons at δ_c 150.56, 146.66 and 137.50 and 139.86 respectively, established the assignments of the above proton signals to its methoxyls at C-4, C-8, C-7 and C-3 respectively. The long-range XHCORR correlations of 1a and 1c are shown on their respective structural diagrams in Figs. 2 and 3. The above 2D nmr spectral data of 1a and 1c, thus unambiguously established their structures proposed from other spectral evidence.

Bulbophyllanthrin (2a) represents a phenanthrene with unusual distributions of the oxygen functions. It is devoid of any oxygen function at C-7, which is usually present in most naturally occurring phenanthrene derivatives, and is characterized by the presence of a hydroxyl at C-5 and a methoxyl at C-4 forming a strong intramolecular hydrogen bond — a structural feature observed for the first time. The structure of the compound proposed from its uv, ir, ^1H

Fig 2 HETCOR contour plot of confusarin (1a) showing 3-bond ^1H - ^{13}C correlationsFig 3 HETCOR contour plot of confusarinid (1c) showing 3-bond ^1H - ^{13}C correlations

and ^{13}C nmr spectral data (Tables 1 and 2) was also confirmed by unequivocal evidence provided by 2D nmr spectral studies.

The homonuclear (^1H - ^1H) correlation experiment (COSY) with **2a** clearly showed a correlation due to 5-bond proton-proton spin coupling between the methoxyl protons at δ 4.07 and the singlet aromatic proton at δ 7.15. This required them to be on adjacent carbon atoms. The assign-

ment of the signal at δ 7.15 to H-1 already made from ^1H and ^{13}C nmr spectral data thus confirmed the placement of the methoxyl group corresponding to the signal at δ 4.07 at C-2 of **2a**. The methoxyl group at δ 3.85, on the other hand, showed no correlation with any aromatic proton, which should therefore be at C-4. The singlet aromatic proton could, however, conceivably be located at C-2 or C-3, instead at C-1, and in view of the polyoxygenated

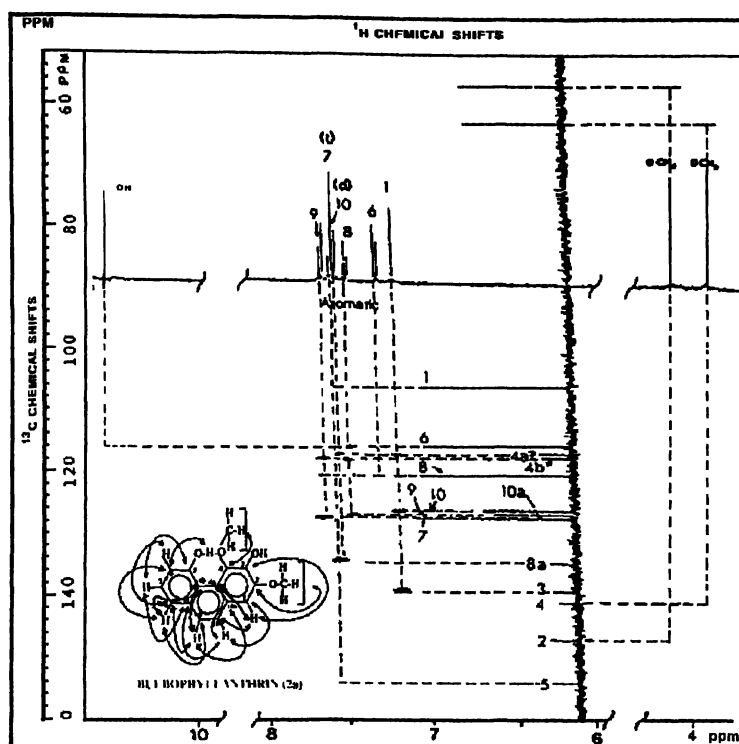


Fig. 4. HETCOR contour plot of bulbophyllanthrin (2a) showing 3-bond ^1H - ^{13}C correlations.

nature of ring-C of **2a**, these alternative formulations cannot be ruled out unequivocally on the basis of the chemical shift data alone.

The heteronuclear (^1H - ^{13}C) correlation plots showing 1-bond correlations arising from direct ^1H - ^{13}C spin-couplings and long-range correlations arising from 2-bond and 3-bond ^1H - ^{13}C spin-couplings provided unambiguous spectral assignments and confirmed the proposed structure of bulbophyllanthrin eliminating all other alternative possibilities. The HETCOR contour plot of **2a** showing 1-bond correlations obtained by using J_{CH} parameter set to 160 Hz established that the protons corresponding to the signals at δ 7.15 (s), 7.26 (dd), 7.42 (dd), 7.51 (app.t) 7.50 (d) and 7.57 (d) were directly linked to the carbon atoms resonating at δ_c 106.0, 115.74, 120.32, 127.43, 126.14 and 126.85 respectively. Thus, identification of the protons from their characteristic resonances would enable the correct assignments of carbon resonances and vice versa. The hydroxyl group at C-5 in **2a** is the only substituent on its ring-A, and H-6, H-7, and H-8 showed a characteristic three-spin coupling pattern for consecutive aromatic protons. Placement of a hydroxyl group at C-5, in **2a** permitted assignment of the signal at δ 7.26 to H-6. Since this proton showed a 1-bond correlation with the carbon at δ_c 115.74, the latter must be assigned to C-6 of **2a**. Unequivocal confirmation

of this assignment was provided by the 3-bond correlation between C-6 and the 5-hydroxyl proton at δ 10.3 (Fig. 4). This left the proton at δ 7.42 with no possible assignment other than H-8, and the 1-bond correlation of this proton with the carbon at δ_c 120.32 implied that the latter must be assigned to C-8. In aromatic systems 3-bond correlations are strong, while 2-bond correlations are not very common and observed only in highly oxygenated aromatic compounds. Consequently C-8 (δ_c 120.32) showed 3-bond correlations with both H-6 (δ 7.26) and H-9. This confirmed the assignment of the signal at δ 7.57 to H-9. Since the proton at δ 7.57 showed 1-bond correlation with the carbon atom at δ_c 126.85, the latter should then be assigned to C-9. This left the signal at δ 7.50 to be assigned only to H-10. Since H-10 exhibited 1-bond correlation with the carbon at δ_c 126.14, this signal must be assigned to C-10. The signal at δ 7.15 was assigned to H-1 which displayed 1-bond correlation with the carbon at δ_c 106.0. The latter should then correspond to C-1. The aromatic proton at δ 7.15 (H-1) showed strong 3-bond correlations with C-10 (δ_c 126.14) and the nonprotonated carbons at δ_c 138.90 and 117.11. This ruled out the other possible structures of **2a** with protons at C-2 or C-3, and also confirmed the assignments of the signals at δ_c 138.90 and 117.11 to C-3 and C-4a, respectively. Other correlations (Fig. 4) allowed

unequivocal assignments of all the carbon atoms of **2a**. Thus, H-10 (δ 7.50) also showed strong 3-bond correlations with C-1 (δ_c 106.0), C-4a (δ_c 117.11) and C-8a (δ_c 134.53). Similarly, 3-bond correlations of H-9 (δ 7.57) with C-8 (δ_c 120.32), C-10a (δ_c 127.34), and C-4b (δ_c 117.69) confirmed the C-8, C-10a, and C-4b resonances. Again, H-8 (δ 7.42) exhibited 3-bond correlations with C-6 (δ_c 115.74), C-4b (δ_c 117.69), and C-9 (δ_c 126.85). H-7 (δ 7.51), as expected, also exhibited 3-bond correlations with both C-5 (δ_c 154.24 and 134.24) and C-8a (δ_c 134.53) confirming the carbon resonances at δ_c 154.24 and 134.53 to be assigned to C-5 and C-8a respectively. The methoxyl protons at δ 4.07 (assigned to OMe at C-2) and 3.85 (OMe at C-4) also showed strong 3-bond correlations with the carbons at δ_c 146.90 and 140.71, which must be assigned to C-2 and C-4 respectively. The 3-bond correlations (HETCOR) observed with **2a** are shown in its structural diagram (Fig. 4). The structure of bulbophyl-lanthrin is thus established as **2a**

Gymnopusin (**1e**) is the first naturally occurring phenanthrene derivative having an oxygen substituent at C-9 and may have several alternative formulations with methoxyl (or hydroxyl) at C-9, which can also be placed at C-10 on the basis of ^1H and ^{13}C nmr spectral data alone. The proposed structure **1e** for gymnopusin was finally established by unequivocal evidence provided by 1-bond and long-range heteronuclear (^1H - ^{13}C) correlation plots obtained from

XHCORR 2D nmr spectral analysis of its diacetyl derivative (**1f**) using J_{CH} parameters set to 160 and 7 Hz respectively (both recorded in a Bruker Supercon 300 MHz instrument). The results also confirmed the ^1H and ^{13}C resonances of the compound. Thus, the XHCORR 1-bond correlation (^1H - ^{13}C) plot of **1f** showed that the signals of the readily identifiable protons H-5 (δ 9.58), H-6 (δ 7.41), and H-8 (δ 8.07) exhibited strong 1-bond correlations with the carbons resonating at δ_c 128.66, 121.36 and 114.03 respectively. This permitted unambiguous assignments of the above signals to C-5, C-6, and C-8 respectively, of **1f**. Similar 1-bond correlations were also discernible between the protons at δ 7.26 and 6.86 with the carbons at δ_c 115.75 and 102.52 respectively. The original assignments¹⁰ of the above proton signals to H-10 and H-1 respectively, of **1f** have now been reversed to H-1 and H-10 respectively. So the carbon signals at δ_c 115.75 and 102.52 must be assigned to C-1 and C-10 respectively. Unequivocal evidence for these assignments was provided by the long-range heteronuclear (^1H - ^{13}C) correlation plot of **1f** (Fig. 5). Thus, the proton at δ 7.26 (H-1) showed strong 3-bond correlations with the carbons at δ_c 142.86, 118.85 and 102.52, which must be assigned to C-3, C-4a, and C-10 respectively, of **1f**. The proton at δ 7.26 (H-1) also exhibited a fairly strong 2-bond correlation with the carbon at δ_c 143.43 which corresponded to C-2. Such 2-bond correlation which is usually not ob-

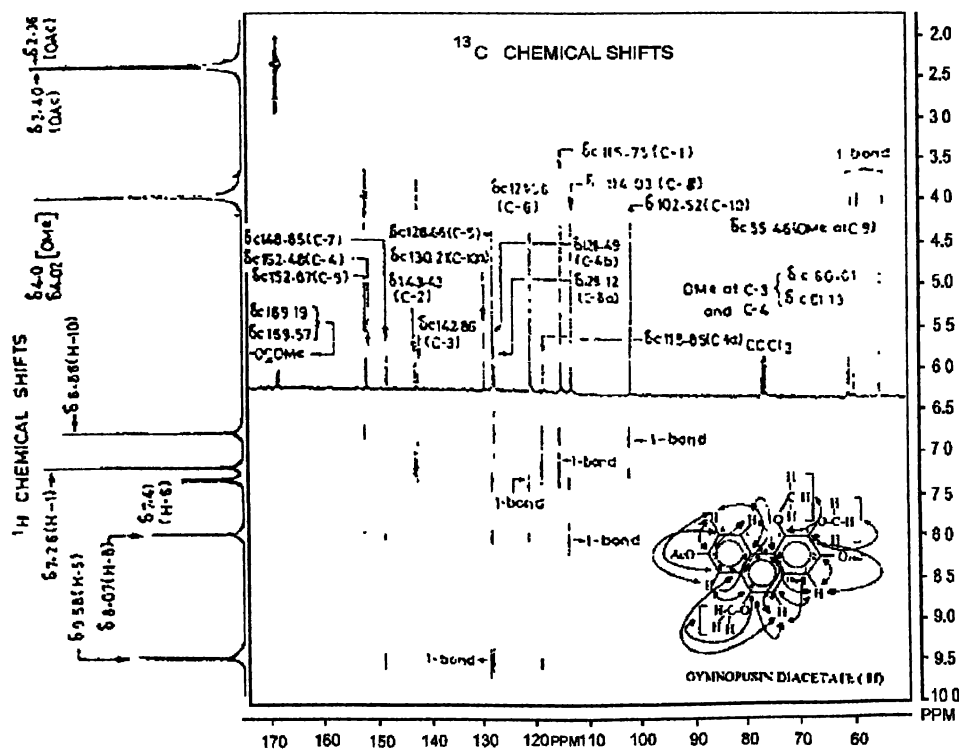


Fig 5 XHCORR 2D contour plot of gymnopusin diacetate (**1f**) showing (3-bond and 2-bond) ^1H - ^{13}C correlations.

served in the aromatic systems is quite interesting and may be assumed to occur due to the presence of oxygenated systems like acetoxy and methoxy attached to the aromatic ring which alter the electron distribution in favour of such coupling. The correlation of the proton at δ 7.26 with two oxygenated carbons at δ_c 142.86 (C-3) and 143.43 (C-2) thus confirmed its assignment to H-1 of **1f**. The earlier assignment¹⁰ of the above signal to H-10 of **1f** failed to account for the above correlations. The other singlet signal at δ_c 6.86 earlier assigned to H-1 of **1f** must then correspond to H-10 which showed 3-bond correlations with the carbons at δ_c 115.75 (C-1), 118.85 (C-4a), and 128.12 (C-8a), besides a 1-bond correlation with the carbon at δ_c 102.52 (C-10) and a fairly strong 2-bond correlation with the carbon at δ_c 152.87 (C-9) which could be assigned to a methoxy bearing carbon atom. This provided the strongest evidence for the placement of a methoxyl group at C-9 of **1f** and hence gymnopusin (**1e**) itself. Another convincing evidence for the placement of a methoxyl group at C-9 of **1f** was provided by a strong 3-bond correlation of the readily identifiable proton H-8 (δ 8.07) of **1f** with the methoxybearing carbon at δ_c 152.87 (C-9). H-8 of **1f** also exhibited strong 3-bond correlations with the carbons at δ_c 128.49 (C-4b) and 121.36 (C-6), besides a 2-bond correlation with C-7 (δ_c 148.85) bearing an acetoxy group, and 1-bond correlation with C-8 (δ 114.03). The long-range correlations of H-6 (δ 7.41) and H-5 (δ 9.58) of **1f** also provided further evidence in favour of its proposed structure. Thus, H-6 (δ 7.41) showed strong 3-bond correlations with C-4b (δ_c 128.49) and C-8 (δ_c 114.03), besides 1-bond correlation with C-6 (δ_c 121.36) and a weak 2-bond correlation with C-7 (δ_c 148.85). H-5 (δ 9.58), likewise, exhibited strong 3-bond correlations with C-7 (δ_c 148.85), C-4a (δ_c 118.85) and C-8a (δ_c 128.12), besides 1-bond correlation with C-5 (δ_c 128.66). The aromatic methoxyl protons at δ 4.0 (6H) and 4.02 (3H) also showed 3-bond correlations with carbons at δ_c 142.86, 152.48, and 152.87, assigned to the methoxy-bearing carbon atoms C-3, C-4, and C-9 respectively. All the 3- and 2-bond ^1H - ^{13}C correlations are depicted in the structural diagram of **1f** (Fig. 5). The structure of gymnopusin diacetate is thus established as **1f** and that of gymnopusin itself as **1e**.

Cirrhopetalanthrin (**3a**) which is the first naturally occurring dimeric phenanthrene derivative, is another interesting compound of biogenetic importance. The structure of the compound including the sites of dimerization (C-1 and C-1') was also established unambiguously by 1-bond and long-range heteronuclear (^1H - ^{13}C) correlation plots of its tetracetyl derivative **3b** obtained from HETCOR 2D experiments using J_{CH} parameters set to 160 and 7 Hz respectively. Thus, the readily identifiable protons H-5 (H-5') [δ 9.77], H-6 (H-6') [δ 7.42] and H-8 (H-8') [δ 7.56] con-

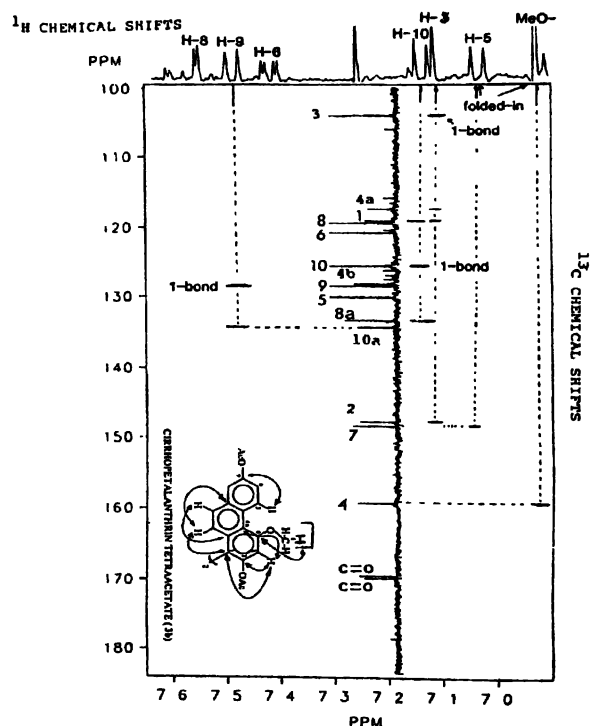


Fig. 6. HETCOR contour plot of cirrhopetalanthrin tetraacetate (**3b**) showing long range (3-bond and 2-bond) ^1H - ^{13}C correlations.

tituting an ABX pattern, and H-9 (H-9') [δ 7.49] and H-10 (H-10') [δ 7.16] representing an isolated AB system of **3b** showed strong 1-bond correlations with the carbons appearing at δ_c 130.18, 120.82, 119.46, 128.50 and 125.65 respectively. This permitted unambiguous assignments of the above carbon resonances of **3b** to C-5 (C-5'), C-6 (C-6'), C-8 (C-8'), C-9 (C-9') and C-10 (C-10') respectively. The singlet proton signal at δ 7.14 assigned to H-3 (H-3') of **3b** also exhibited a similar 1-bond correlation with the carbons resonating at δ_c 104.07 which should then correspond to C-3 (C-3') of the compound. Most convincing evidence for the structure of **3b** and hence for cirrhopetalanthrin (**3a**) itself was provided by the long-range HETCOR analysis of **3b** utilizing the results obtained from the above 1-bond correlation experiment. Thus, the aromatic protons resonating at δ 7.14 [already assigned to H-3 (H-3') of **3b**] showed strong 3-bond correlations with both C-1 (C-1') [δ_c 119.18] and C-4a (C-4a') [δ_c 117.53] (Fig. 6) in addition to the 1-bond correlation which sometimes is also observed in long-range experiments. The above protons also showed a fairly strong 2-bond correlation with C-2 (C-2') [δ_c 147.84], which is quite interesting as stated earlier in connection with similar observation with gymnopusin diacetate (**1f**). The protons at δ 7.16 [H-10 (H-10')] of **3b** likewise exhi-

bited strong 3-bond correlations with both nonprotonated carbons C-1 (C-1') [δ_c 119.18] and C-8a (C-8a') [δ_c 133.50], besides 1-bond correlation with C-10 (C-10') (Fig. 6) confirming the dimerization to take place through C-1 of two identical phenanthrene units. Similar 3-bond correlations between H-9 (H-9') [δ 7.49] and C-10a (C-10a') [δ_c 134.39] and H-5 (H-5') [δ 9.77] and C-7 (C-7') [δ_c 148.48] of **3b** were also observed. The carbon atoms C-4 (C-4') of **3b** bearing the methoxyl groups exhibited an intense 3-bond correlation with the folded-in methoxyl protons (δ 4.25), and this confirmed the signal at δ_c 159.18 to be assigned to these carbon atoms. The structure of cirrhopenetanthrin tetraacetate is thus established as **3b**, which, in turn, confirmed the structure of cirrhopenetanthrin as **3a**.

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