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REVISED STRUCTURE OF POLYAVOLENSIN AND ITS ANALOGUES

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Abstract—The structure of polyavolensin (4) has been determined by X-ray crystallography and the recently published structure needs revision.

THE three new indolosesquiterpenoid alkaloids polyavolensin, polyavolensinol and polyavolensinone were recently isolated[2] from the medicinal plant *Polyathia suaveolens* Engl & Diels. On the basis of spectroscopic data and chemical interconversions the constitutions (**1**, **2** and **3**) respectively were proposed for these three compounds.

A single crystal X-ray crystallographic study has now shown that the proposed structure of polyavolensin (**1**) should be revised to **4**, accordingly polyavolensinol and polyavolensinone are now represented by **5** and **6** respectively.

A suitable crystal for X-ray investigation was obtained by slow evaporation of a hexane solution of polyavolensin. *Crystal data.* $C_{25}H_{33}NO_2$, M = 379.5, Hexagonal, a = 10.187(3), c = 71.58(1) Å U = 6433 Å,^{3} D_c = 1.17 g cm^{-3}, Z = 12, Space group $P6_122$ (or $P6_522$), Mo-K_α radiation λ = 0.7106 Å.

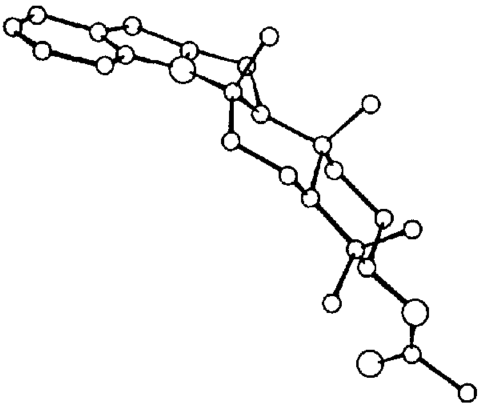
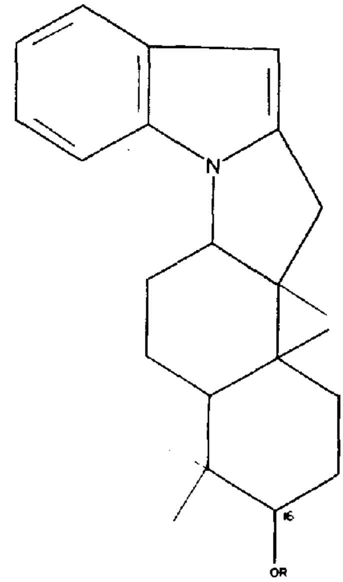


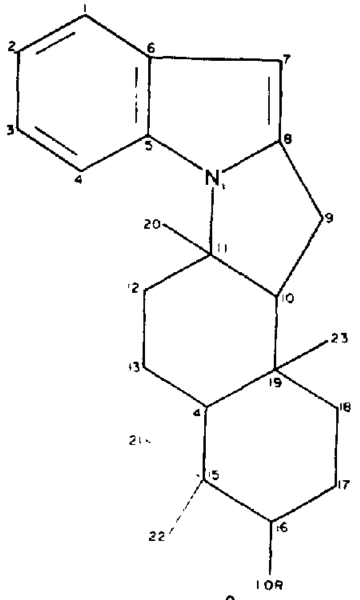
Fig. 1.



(1) R=Ac

(2) R=H

(3) 16 Ketone



(4) $R = Ac(-\overset{\overset{O_2}{\|}}{\underset{24}{C}}-\underset{25}{CH_3})$

(5) R=H

(6) 16 Ketone

Table 1. Interatomic distances (Å); standard deviations 0.01 Å

C(1) - C(2)	1.39	C(9) - C(10)	1.53	C(15) - C(21)	1.53
C(1) - C(6)	1.43	C(10) - C(11)	1.54	C(15) - C(22)	1.54
C(2) - C(3)	1.39	C(10) - C(19)	1.53	C(16) - C(17)	1.52
C(3) - C(4)	1.41	C(11) - N(1)	1.49	C(16) - O(1)	1.45
C(4) - C(5)	1.39	C(11) - C(12)	1.51	C(17) - C(18)	1.52
C(5) - C(6)	1.39	C(11) - C(20)	1.56	C(18) - C(19)	1.52
C(5) - N(1)	1.39	C(12) - C(13)	1.56	C(19) - C(23)	1.55
C(6) - C(7)	1.44	C(13) - C(14)	1.55	O(1) - C(24)	1.33
C(7) - C(8)	1.37	C(14) - C(15)	1.56	C(24) - O(2)	1.21
C(8) - N(1)	1.37	C(14) - C(19)	1.57	C(24) - C(25)	1.48
C(8) - C(9)	1.54	C(15) - C(16)	1.54		

Table 2. Bond angles (°); standard deviations in parentheses

C(1) - C(2) - C(3)	121.9(9)	C(14) - C(15) - C(16)	106.3(7)
C(2) - C(3) - C(4)	122.3(9)	C(14) - C(15) - C(21)	109.3(6)
C(3) - C(4) - C(5)	115.3(9)	C(14) - C(15) - C(22)	113.3(7)
C(4) - C(5) - N(1)	129.3(9)	C(21) - C(15) - C(22)	108.3(8)
C(4) - C(5) - C(6)	124.3(7)	C(21) - C(15) - C(16)	107.4(8)
N(1) - C(5) - C(6)	106.2(8)	C(22) - C(15) - C(16)	112.2(6)
C(5) - C(6) - C(1)	118.7(9)	C(15) - C(16) - C(17)	114.3(8)
C(1) - C(6) - C(7)	132.0(9)	C(15) - C(16) - O(1)	108.6(7)
C(5) - C(6) - C(7)	109.4(7)	O(1) - C(16) - C(17)	109.1(6)
C(6) - C(7) - C(8)	104.6(8)	C(16) - C(17) - C(18)	110.9(7)
C(7) - C(8) - N(1)	111.3(7)	C(17) - C(18) - C(19)	113.0(7)
C(7) - C(8) - C(9)	140.5(9)	C(18) - C(19) - C(14)	109.0(7)
N(1) - C(8) - C(9)	108.2(8)	C(18) - C(19) - C(10)	108.5(7)
C(8) - C(9) - C(10)	97.7(7)	C(18) - C(19) - C(23)	109.4(6)
C(9) - C(10) - C(11)	105.7(7)	C(23) - C(19) - C(10)	111.8(7)
C(9) - C(10) - C(19)	122.3(7)	C(23) - C(19) - C(14)	115.4(7)
C(11) - C(10) - C(19)	116.2(7)	C(10) - C(19) - C(14)	102.5(6)
C(10) - C(11) - N(1)	96.1(6)	C(16) - O(1) - C(24)	118.6(8)
C(10) - C(11) - C(20)	117.0(6)	O(1) - C(24) - O(2)	123.1(9)
C(10) - C(11) - C(12)	109.8(7)	O(1) - C(24) - C(25)	112.8(11)
N(1) - C(11) - C(20)	106.5(7)	O(2) - C(24) - C(25)	124.1(11)
N(1) - C(11) - C(12)	114.3(6)	C(5) - N(1) - C(8)	108.5(7)
C(20) - C(11) - C(12)	112.2(8)	C(5) - N(1) - C(11)	138.2(7)
C(11) - C(12) - C(13)	109.6(7)	C(8) - N(1) - C(11)	113.1(6)
C(12) - C(13) - C(14)	111.7(8)	C(13) - C(14) - C(19)	111.6(7)
C(13) - C(14) - C(15)	115.2(7)	C(19) - C(14) - C(15)	116.4(5)

Table 3. Devaitions (Å); from the mean plane through C(1)–C(6)

C(1)	-0.002	C(8)	0.092	C(12)	0.922	C(19)	1.139
C(2)	0.007	C(9)	0.219	C(13)	1.254	C(20)	-1.380
C(3)	-0.005	C(10)	0.846	C(14)	2.025	C(21)	3.825
C(4)	-0.001	N(1)	0.094	C(15)	2.792	C(22)	1.860
C(5)	0.006	O(1)	4.192	C(16)	3.531	C(23)	-0.161
C(6)	-0.005	O(2)	5.993	C(17)	2.667	C(24)	5.370
C(7)	0.037	C(11)	0.102	C(18)	1.974	C(25)	5.839

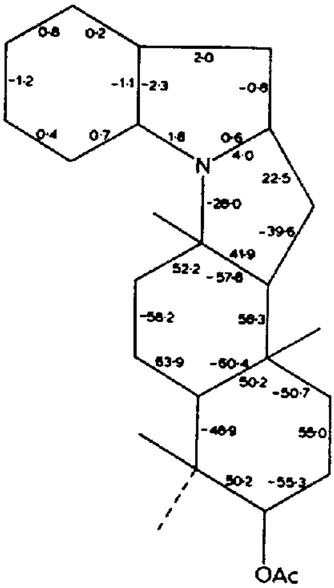


Fig. 2.

Data was collected on a Hilger and Watts Y290 diffractometer for $\theta \leq 23°$ giving a total of 1955 unique reflections of which 1107 had $I > 3\sigma I$ and were used in the refinement. The structure was solved routinely by Multan[3] which revealed all the non-H atoms. Refinement and other crystallographic compilations were done using the Crystals package. At a late stage in the refinement all but two of the H atoms were located in a difference map and were afterwards included (but not refined) in calculated positions (or where this was not possible, in found positions). The final conventional R value at convergence was 6.65%.

Bond lengths and bond angles are shown in Tables 1 and 2 (the crystallographic numbering scheme is indicated in 4), while Fig. 1 shows a computer generated perspective diagram of polyavolensin drawn using the final atomic co-ordinates. Representation of the relative configuration only is intended in Fig. 1, the absolute configuration of polyavolensin was not determined in the present study. A recent X-ray crystallographic study[4] of the related alkaloid polyveoline as its hydrochloride indicates that probably the absolute configuration of polyavolensin is opposite that shown in Fig. 1. It is clear that the indole system is substantially planar, in fact the maximum deviation from the mean plane containing C1–C6 is only 0.09 Å (Table 3). Selected torsion angles are included in Fig. 2. The pyrrolidine ring has an envelope conformation, while the *trans*-fused decalin system has the expected chair–chair conformation.

The biogenesis of polyavolensin (4) can now be accommodated within the scheme outlined by Wenkert[5] for polyalthenol. In the case of polyavolensin however the initial β-substitution of a tryptophane derived indole must be followed by migration[6] of the sesquiterpenoid residue to the α position, and this is followed by cyclisation to give the pyrrolidine ring.

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