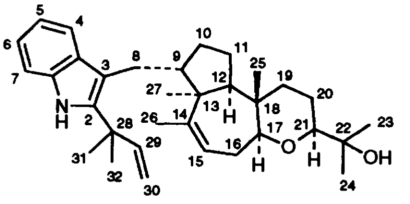
Structure of a New Type of Indoloditerpenoid from *Emericella purpurea*

Ken-ichi Kawai,* Koohei Nozawa and Shoichi Nakajima
Faculty of Pharmaceutical Sciences, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

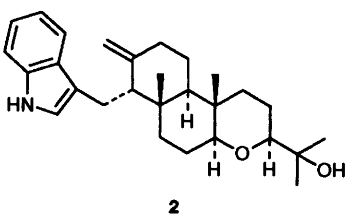
The structure and relative stereochemistry of a new type of indoloditerpenoid designated as emindole PA 1, isolated from the mycelium of *Emericella purpurea*, along with the sesterterpene variecolin recently isolated from *Emericella variecolor*, has been confirmed by a chemical and spectroscopic investigation.

During a search for fungal indoloditerpenoids, two components, one with a bluish and the other a reddish colouration when sprayed with van Urk reagent[1] were detected on TLC, in the dichloromethane extract of *Emericella purpurea* Samson & Mouchacca, strain IFO 30849, which was isolated from Egyptian desert soil.[2] The former compound was identical with variecolin, a sesterterpene recently isolated from *E. varievolor* Berkeley & Broome was shown to be an angiotensin II receptor binding inhibitor,[3] whereas the latter was a new compound which we designated as emindole PA 1.

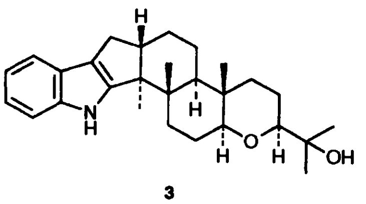
The molecular formula of 1 was confirmed by high resolution electron-impact ionization (EI) mass spectrometry as $C_{33}H_{47}NO_2$. A positive colouration with van Urk reagent (reddish purple)[1] and the fragment ion at *m*/*z* 130 [$(C_9H_8N)^+$, 12%] in the EI mass spectra suggested the presence of an indole moiety. The ^1H NMR spectrum of 1 was similar to that of emindole DB 2, which has been isolated from *E. desertrum* Samson & Mouchacca,[4] except for the appearance of signals assigned to a 1,1-dimethylallyl residue [δ_H 6.12 (1 H, dd), 5.13 (1 H, d), 5.15 (1 H, d), 1.34 (3 H, s) and 1.53 (3 H, s)] and a vinylic proton [δ_H 5.53 (br d, *J* 5.9 Hz)] instead of those of the *exo*-methylene (δ_H 4.18 and 4.51) in 2. The presence of the much stronger fragment ion of *m*/*z* 198 [$(C_{14}H_{16}N)^+$, 100%] than that of *m*/*z* 130 in the EI mass spectra in 1 indicated an alkylated indole moiety. The presence of four aromatic protons [δ_H 7.50 (br d), 7.03 (br t), 7.10 (br t) and 7.25 (br d)] and the above data showed the presence of a 2-(1,1-dimethylallyl)indol-3-ylmethyl group.



1



2



3

Table 1 ^1H and ^{13}C NMR assignment for emindole PA 1

Carbon no.	δ_C	δ_H (*J*/Hz)	COLOC correlation
1 (NH)		7.82 br s	
2	147.1 s		31-H
3	110.5 s		1-H (NH)
3a	130.4 s		1-H (NH), 8-H
4	119.3 d	7.50 br d (7.7)	
5	118.8 d	7.03 br t (7.7)	7-H
6	121.1 d	7.10 br t (7.7)	4-H
7	110.1 d	7.25 br d (7.7)	
7a	134.4 s		
8	25.6 t	2.64 dd (14.1 12.1) 3.06 dd (14.1, 3.3)	10-H
9	46.5 d	1.65 dddd (12.1, 12.1, 3.7, 3.3)	27-H
10	26.8 t	1.27 dddd (13.2, 12.9, 12.1, 3.2) 1.43 m	
11	25.9 t	0.87 dddd (13.2, 13.2, 12.8, 3.7) 1.60 m	
12	45.6 d	1.89 br d (12.8)	25-H
13	39.8 s		10-H, 27-H
14	139.3 s		
15	114.0 d	5.53 br d (5.9)	
16	28.8 t	1.97 br dd (15.8, 10.6) 2.07 ddd (15.8, 5.9, 5.5)	
17	79.9 d	3.21 dd (10.6, 5.5)	
18	34.4 s		25-H
19	36.4 t	1.17 ddd (13.2, 12.8, 4.3) 1.85 ddd (12.8, 3.7, 3.3)	25-H
20	22.1 t	1.43 m 1.47 dddd (13.2, 11.4, 10.8, 3.7)	
21	83.9 d	3.13 dd (10.8, 2.6)	23-H, 24-H
22	71.8 s		23-H, 24-H
22-OH		2.66 br s	
23	23.8 q	1.14 s	
24	26.0 q	1.16 s	
25	13.2 q	0.71 s	
26	28.0* q	1.53 s	
27	23.3 q	1.04 s	
28	39.3 s		32-H
29	146.6 d	6.12 dd (17.1, 10.6)	32-H
30	111.7 t	5.13 d (10.6) 5.15 d (17.1)	
31	25.5 q	1.34 s	
32	27.8* q	1.53 s	

From a detailed analysis of the ^1H–^1H and ^1H–^{13}C shift correlation spectra and the long-range shift correlation (COLOC) spectrum, the carbon skeleton of emindole PA was determined as 1. The assignments of the ^1H and ^{13}C NMR signals are summarized in Table 1. From the analysis of the correlation peaks in the ^1H–^1H nuclear Overhauser effect correlation (NOESY) spectrum (Fig. 1), the stereochemistry in 1 was determined. The structure and relative stereochemistry of emidole PA was consequently confirmed as that shown 1.

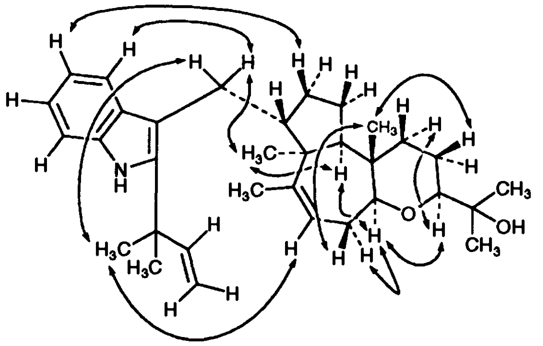


Fig. 1 The correlation peaks in the NOESY spectrum of emindole PA 1

Acklin *et al.*[5] reported that indoloditerpenes such as paspaline **3** were derived from tryptophan and geranylgeraniol with skeletal rearrangement during the biosynthetic process in *Claviceps paspali* Stevens & Hall, whereas emindole DB **2** was derived without such a rearrangement. The biosynthesis of emindole PA **1** involves an additional carbon bond migration step [from C(12)–C(14) to C(12)–C(13)] from the same intermediate as **3**.

Emindole PA **1** is the first example of an indoloditerpenoid bearing a 1,1-dimethylallyl residue at C-2 of the indole moiety.

References

1 E. Stahl and E. Kaldeway, *Hoppe-Zeiler's Z. Physiol. Chem.*, 1961, **323**, 182.
2 Institute for Fermentation (ed.), *List of Cultures* (*IFO*), 9th edn., Osaka, 1992, p. 299.
3 O. D. Hensens, D. Zink, J. M. Williamson, V. J. Lotti, R. S. L. Chang and M. A. Goetz, *J. Org. Chem.*, 1991, **56**, 3399.
4 K. Nozawa, S. Nakajima, K. Kawai and S. Udagawa, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1689.
5 W. Acklin, F. Weibel and D. Arigoni, *Chimia*, 1977, **31**, 63.

Paper 4/01870B
Received 29*th March* 1994
Accepted 5*th May* 1994