





TABLE 1 :  $^{13}\text{C}$  and  $^1\text{H}$  NMR data  $(\text{CD}_3)_2\text{CO}$  for Perforatin

Carbon	c	H <sup>A</sup>	Carbon	c	H <sup>A</sup>
1	152.46	7.36,d,J <sub>1,2</sub> 9.8 HZ	15	58.83	4.67,S
2	119.04	5.88,d,J <sub>2,1</sub> 9.8 HZ	16	166.22	
3	161.11		17	78.51	5.71,br S
4	89.85		20	122.08	
5	80.83		21	142.59	7.65,dt,J <sub>21,23</sub> 1.6,J <sub>21,22</sub>
6	202.88				0.8, J <sub>21,17</sub> 0.8 HZ
7	100.96		22	110.96	6.53,ddd,J <sub>22,23</sub> 1.9
8	52.31				J <sub>22,21</sub> 0.8,J <sub>22,17</sub> 0.4 HZ
9	36.25	3.19-3.25,m	23	144.16	7.6 1,ddd, J <sub>23,22</sub> 1.9, J <sub>23,21</sub> HZ
					1.9, J <sub>23,17</sub> 0.4 HZ
10	44.96				
11	15.70	1.85-1.99,m,2.16-2.28,m		Me (x2)	28.01 1.44,S 1.23 B,S
12	25.98	1.52-1.62, m, 1.80-1.93,m		Me	19.86 1.20 B,S
13	40.59			Me	19.63 1.38, S
14	71.39			Me	15.43 1.21 B,S

<sup>A</sup> H 6.48,OH    <sup>B</sup> May be interchanged.

If it is assumed that perforatin arises from the same ring A cleaved precursor **7** as harrisonin then the above data can be accommodated by structure **8** for the A and B rings. This proposal was vindicated by the determination of the X-ray crystal structure of perforatin which yielded the stereochemistry shown in structure **3**. Perforatin thus joins the strange and much-altered limonoids of the obacunal group (4) in which both rings A and D are cleaved. It is of interest that the stereochemistry of perforatin at C-5 is opposite to that of harrisonin (8). Harrisonin is unlikely to be an artefact (7), but its circular dichroism is anomalous (5) so that the stereochemistry of harrisonin at C-5 may be incorrect or it may arise from a different stereochemical precursor to perforatin.

**Acknowledgement :** we thank Dr Tran Dinh Dai of the Institute of Ecology and Natural Resources of the National Centre for Scientific Research of Vietnam, for the collection and identification of the plant material, Dr. J.K. Macleod for the mass spectrum, the International Foundation for Science, the Australian Research Council, the Australian IDP Network for the Chemistry of Biologically Important Natural Products for financial support.

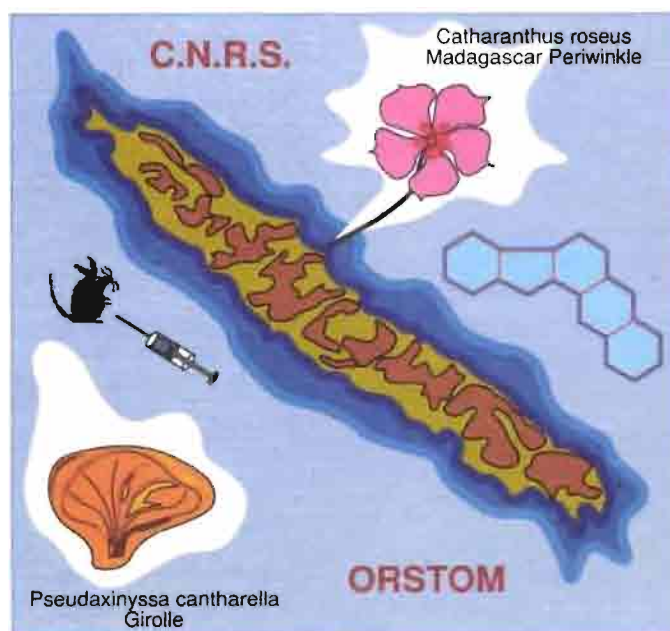
#### References

1. Meixin W. *et al*, *Yaouxuebao* **19**, 10, 760 (1984)
2. Pittaya Tuntiwachwuttikul, *Silpakorn University, Wakorn Pathom, Thailand.*
3. Mai Van Tri *et al*, *J. Nat. Prod.* **44**, 279 (1981)
4. Dreyer D.L. *et al*, *Tetrahedron* **32**, 2367 (1976)
5. Kubo I. *et al*, *Heterocycles* **5**, 485 (1976)
6. Macleod J.K. *et al*, *J. Nat. Prod.* **52**, 882 (1989)
7. Liu H.W., Kubo I. and Nakanishi K., *Heterocycles* **17**, 67 (1982)
8. We thank Pr. Jack Cannon of the University of Western Australia for this observation.

# Troisième Symposium sur les substances naturelles d'intérêt biologique de la région Pacifique-Asie

Nouméa, Nouvelle-Calédonie, 26-30 Août 1991

## ACTES



Editeurs : Cécile DEBITUS, Philippe AMADE,  
Dominique LAURENT, Jean-Pierre COSSON