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THE CONFIGURATION OF VENOTERPINE

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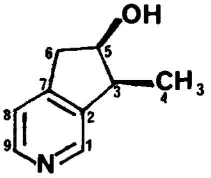
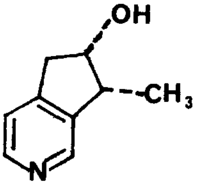
Abstract : Venoterpine and cantleyine were chemically correlated and shown to have the same absolute configuration.

Venoterpine 1[1] and cantleyine 2[2] are monoterpene alkaloids of wide natural distribution[3]. The structure of 2 was proved by a chemical correlation with loganin[2] but the absolute configuration of 1 so far rests only a CD study[4]. Until now it was generally believed albeit without explanation that venoterpine 1 had the opposite configuration from that of cantleyine 2. This situation has recently been questioned[5] and the simultaneous isolation in our laboratory of 1 and 2 in the same plants lead us to reexamine the situation.

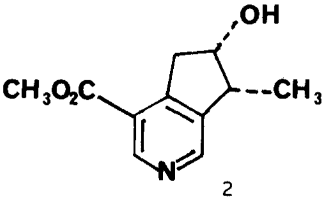


1 previous assignement



1 revised configuration

venoterpine (RW47)



2

cantleyine

Compounds 1 and 2 were isolated from *Alstonia angustiloba*, *A.pneumatophora* and *A.spatulata*[6]. Their gross structures were established by comparison of their physical properties(+) with literature data[1,2]. Examination of their ^{13}C NMR spectra disclosed a similar substitution pattern for their cyclopentane ring (Table I). All these data confirmed the known relative configuration of 1 and 2, the absolute configuration of 1 only remaining to be determined. This was established by a chemical correlation between 2 and 1 based on the flash pyrolysis of the carboxylic acid derived from cantleyine. Barium hydroxide hydrolysis of 2 ($[\alpha]_D$=-40°;$CHCl_3$) followed by CO_2 neutralization yielded an acid, which was dissolved in THF (2mg/ml) and submitted to vacuum flash pyrolysis in a vertical hot tube (glass beads filling) preheated to 460°C. Condensation of the eluate yielded tars and a single non-polar compound in all respects identical to venoterpine (MS, IR, NMR, UV, TLC). The optical rotation of this material ($[\alpha]_D$=+38°;$CHCl_3$) was identical to the value found for natural 1 ($[\alpha]_D$=+32°;$CHCl_3$) within *experimental error*.

We thus conclude that 1 and 2 have the same absolute configuration as loganin, which is probably their common genitor.

Table I : ^{13}C NMR ($CDCl_3$) (δppm)[7]

C	1	2	3	4	5	6	7	8	9	$\underline{C}OOCH_3$	$COO\underline{CH_3}$
1[7]	146,9	142,0	42,5	11,9	74,6	40,7	150,9	120,2	144,6		
1	147,6	142,0	42,8	12	75,1	41	150,6	120,5	145,2		
2	148,8	143,4	42,6	12,1	74,4	42,2	154	123,2	147,1	166,1	52,1

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6. Plant material was kindly provided by Dr T.Sévenet and collected as part of a C.N.R.S. mission in South East Asia.
7. see : M.R.Roby and F.R.Stermitz, J.Nat.Prod., 47, 846 (1984), for the ^{13}C NMR spectra of an isomer of 2 and A.Patra, A.K.Mukhopadhyay and A.K.Mitra, Indian J.Chem., 17B, 175 (1979) for a previous ^{13}C assignment of 1.

(+) ($[\alpha]_D$, UV, IR, SM, ^1H RMN).

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