NEW SECOCULARINE ALKALOIDS FROM SARCOCAPNOS SPECIES

Luis Castedo, Domingo Domínguez, Susana López, Emilia Tojo, and Carmen Villaverde

Departamento de Química Orgánica de la Facultad de Química y Sección de Alcaloides del CSIC, Santiago de Compostela, Spain

Abstract - Five new secocularine alkaloids have been isolated from Sarcocapnos species and their structures elucidated by spectroscopic studies and chemical correlations.

We have previously reported[1] the isolation (from Sarcocapnos crassifolia and Corydalis claviculata) of the first two members of a new group of cularine-related alkaloids which we named secocularines. We report here the isolation from Sarcocapnos crassifolia (Desf.) DC and Sarcocapnos enneaphylla (L.) DC of five new members of this group: secosarcocapnine 1, secosarcocapnidine 2, norsecocularidine 3, norsecosarcocapnine 4 and norsecosarcocapnidine 5. All were obtained as very minor alkaloids, and attempts to crystallize them were unsuccessful; only secosarcocapnine 1 and secosarcocapnidine 2 can be crystallized as their hydrochloride (mp: 168-88°C and 240-41°C, ethanol-ether, respectively).

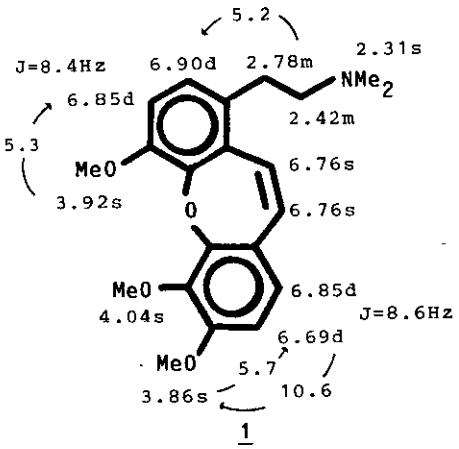
The secocularine nature of the new alkaloids was deduced on the basis of the PMR spectra[2] (Figure I). These show characteristic signals in the aliphatic region which suggested the presence of a $CH_2CH_2NMe_2$ side chain in compounds 1 and 2, and CH_2CH_2NHMe chain in compounds 3, 4 and 5. This interpretation was supported by the presence of base peaks in the mass spectra at m/z 58 ($CH_2=\overset{+}{N}Me_2$) and 44 ($CH_2=\overset{+}{N}HMe$) respectively.

Data for all compounds are summarized in Figure II.

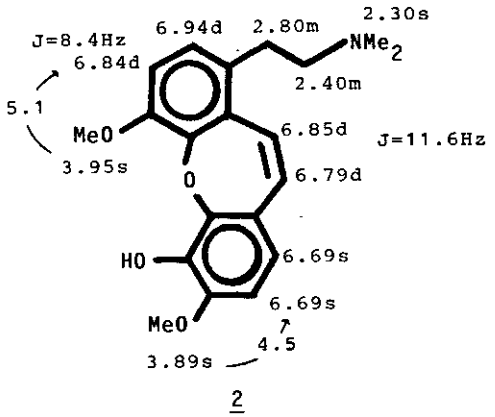
The structures of secosarcocapnine 1 and secosarcocapnidine 2 were confirmed by direct comparison (tlc, PMR, MS) with synthetic products obtained by Hofmann elimination from the corresponding cularine methiodides[3].

The structures of norsecocularidine 3, norsecosarcocapnine 4 and norsecosar-

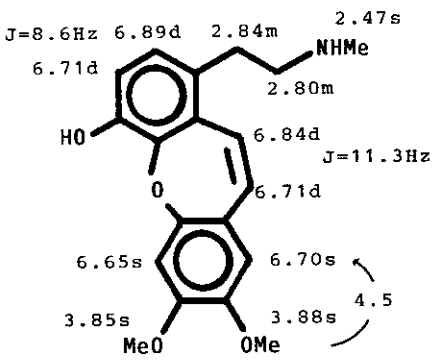
FIGURE I



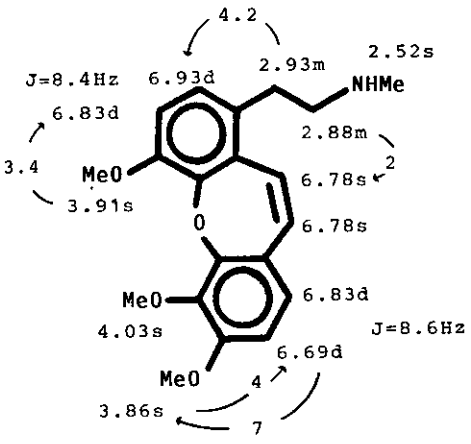
1



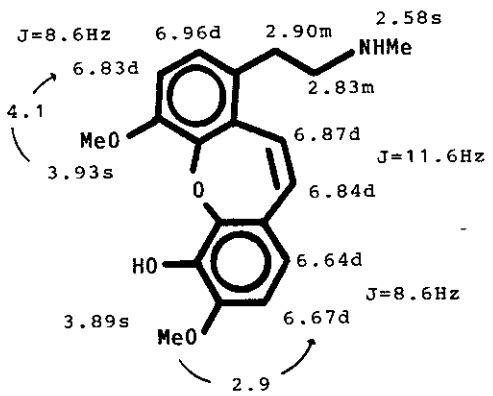
2



3



4



5

cocapnidine 5 were confirmed by transformation into their respective secocularines[1] and secoisocularines via N-methylation with H-COH/$NaBH_4$.

FIGURE II

COMPOUNDS	FORMULA	HIGH-RESOLUTION MS Calcd.	Found	UV	IR cm^{-1}
Secosarcocapnine 1	$C_{21}H_{25}NO_4$	355.178	355.179	λ_{max}^{EtOH} (log ε): 206(4.1), 219(3.9), 246(3.7), 312(3.7).	----
Secosarcocapnidine 2	$C_{20}H_{23}NO_4$	341.162	341.166	λ_{max}^{EtOH} (log ε): 214(3.9), 314(3.6). $\lambda_{max}^{EtOH/OH^-}$ (log ε): 226(4.1), 280(3.6), 310(3.6), 350(3.5).	3400
Norsecocularidine 3	$C_{19}H_{21}NO_4$	327.146	327.146	λ_{max}^{EtOH} (log ε): 219(4.0), 234(4.0), 296(3.5), 318(3.6). $\lambda_{max}^{EtOH/OH^-}$ (log ε): 227(4.2), 322(3.7).	3360
Norsecosarcocapnine 4	$C_{20}H_{23}NO_4$	341.162	341.163	λ_{max}^{EtOH} (log ε): 222(3.6), 244(3.5), 310(3.6).	3400
Norsecosarcocapnidine 5	$C_{19}H_{21}NO_4$	327.146	327.147	λ_{max}^{EtOH} (log ε): 222(3.9), 264(3.6), 284(3.6), 314(3.8). $\lambda_{max}^{EtOH/OH^-}$ (log ε): 228(4.1), 264(3.7), 284(3.6), 314(3.6), 350(3.5).	3420

ACKNOWLEDGEMENTS

We thank the CAICYT (Spain) for its financial support and the Midwest Center for Mass Spectrometry (Department of Chemistry, University of Nebraska, USA) the high-resolution mass spectra provided.

REFERENCES AND NOTES

1. J.M.Boente, L.Castedo, D.Domínguez, A. Fariña, A.Rodriguez de Lera, and M.Carmen Villaverde; Tetrahedron Lett.. 1984, 25, 889.

2. All the PMR spectra including NOE difference studies were recorded at 250 MHz in $CDCl_3$ solution with TMS as internal standard. All the data are summarized on the corresponding structures in Figure I. Chemical shifts of norsecocularines 3, 4 and 5 are slightly concentration depending.

3. This reaction, first carried out by R.H.F.Manske in his work on the structure of cularine (J.Am.Chem.Soc., 1950, 72, 55) gave elimination material of unknown composition. Our experiments, using sodium ethoxide in refluxing ethanol for 3 hours, gave the secocularines 1 and 2 in 80% yield.

Received, 26th September, 1986