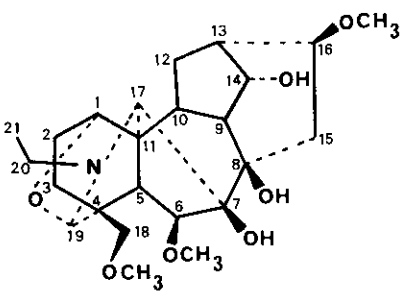
18-METHOXYGADESINE, A NEW DITERPENOID ALKALOID

Antonio G. González*, Gabriel de la Fuente, and Obdulia Munguía

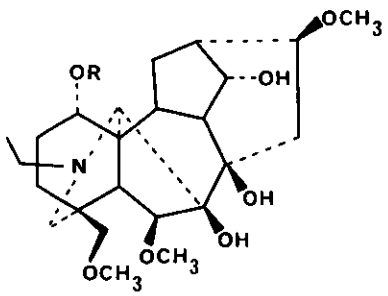
Instituto Universitario de Química Orgánica, Universidad de La Laguna; Instituto de Productos Naturales Orgánicos, CSIC, La Laguna, Tenerife, Spain

Abstract - The structure of 18-methoxygadesine has been determined on the basis of its spectral data and chemical correlation with delcosine.

During our studies of diterpenoid alkaloids from Consolida orientalis Gay[1] we have isolated 18-methoxygadesine (1) as a minor constituent.



1



2 R = CH_3

3 R = H

The new base had m.p. 180-184°C. Its MS is characteristic of those alkaloids with a lycoctonine skeleton, giving the molecular ion at M^+ 451.2566 amu (1%), $C_{24}H_{37}NO_7$, (calcd. 451.2570) and fragments at M^+-CH_3 (100%), M^+-CH_3O (6%), $|M^+-CH_3|-H_2O$ (30%) and 395.2289 (3%), $M^+-C_3H_4O$ (calcd. 395.2308), which indicated the presence of the C-1-C-9 inner ether[2]. Moreover, the IR spectrum showed absorptions at 895 and 1000 cm^{-1}, proper of such a function[3]. The ^{1}H-NMR (Cl_3CD) displayed signals at δ1.09 (3H, t, J 7 Hz, N-CH_2-CH_3), 3.30, 3.90, 3.41 (3H each, s, three OCH_3), 3.70 (1H, m, $W_{\frac{1}{2}}$ = 7 Hz, C-1βH), 4.13 (1H, t, J 5 Hz, C-14βH), 3.88 and 3.95 (1H each, s), which could be assigned to either C-6αH or C-19H.

The ^{13}C-NMR is similar to that of browniine (2)[4] and delcosine (3)[5].

^{13}C Chemical shifts and assignments

Carbon	1	2	3	Carbon	1	2	3
1	85.23	85.2	72.7	13	45.33	46.1	45.3
2	21.90	25.5	27.5	14	75.35	75.3	75.8
3	25.50	32.5	29.4	15	33.85	33.1	34.5
4	43.16	38.4	37.6	16	81.70	81.7	82.0
5	38.19	45.1	44.0	17	64.09	65.4	66.3
6	90.22	90.1	90.1	18	73.35	78.0	77.4
7	85.12	89.1	87.9	19	68.80	52.7	57.1
8	76.14	76.3	78.1	20	47.38	51.3	50.4
9	49.56	49.6	45.3	21	13.68	14.3	13.7
10	36.85	36.4	39.4	1'		56.0	
11	46.44	48.2	48.9	6'	58.87	57.5	57.4
12	27.75	27.5	29.4	16'	56.51	56.5	56.4
				18'	59.08	59.1	59.1

Chemical shifts in ppm downfield from TMS.

Solvent deuterochloroform.

The new doublet at 68.80 ppm, the singlet at 43.16 ppm and the γ effects observed on the resonances of C-3, C-5 and C-18, are consistent with a C-1-C-9 inner ether in (1). Oxidation of delcosine with $KMnO_4$[6] led to our base (1) (m.p., IR, ^1H-NMR and MS identical).

The pairs of alkaloids 18-methoxygadesine-delcosine and 18-hydroxy-14-O-methyl-gadesine-gigactonine isolated in this plant[1], as in a similar work on Delphinium pentagynum[7], confirm the possible existence of other such pairs in nature, at least as minor constituents.

ACKNOWLEDGEMENTS

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