# 18-METHOXYGADESINE, A NEW DITERPENOID ALKALOID

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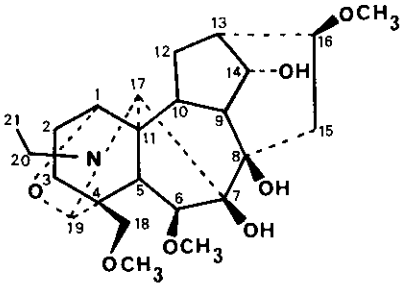
Abstract - The structure of 18-methoxygadesine has been determined on the basis of its spectral data and chemical correlation with delcosine.

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



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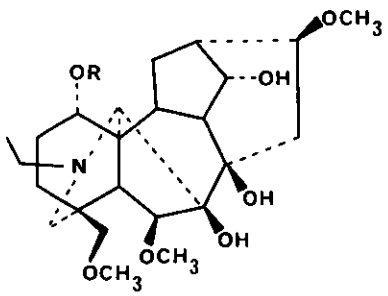

2 R = $CH_3$

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 $\gamma$ 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.

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