

STRUCTURE OF 18-HYDROXY-14-O-METHYLGADESINE

A NEW DITERPENE ALKALOID FROM *CONSOLIDA ORIENTALIS*

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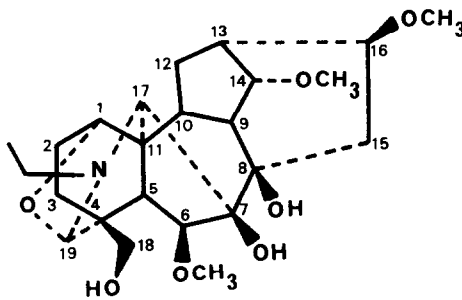
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Summary.— The structure of 18-hydroxy-14-O-methylgadesine, isolated from *Consolida orientalis*, was determined by spectroscopic methods and X-ray crystallography.

From *Consolida orientalis* Gay, subsp. *orientalis* (syn. *Delphinium orientale* Gay; incl. *D. hispanicum* Wilk.)¹, we have isolated a new diterpene alkaloid, 18-hydroxy-14-O-methylgadesine (I), in a very small amount.

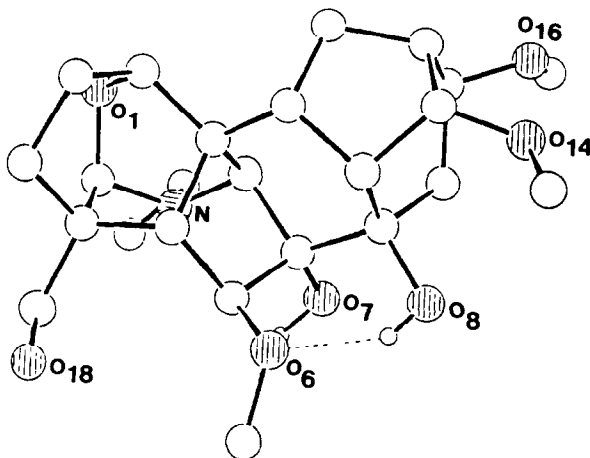


I

18-Hydroxy-14-O-methylgadesine had m.p. 110 - 114°C. The MS is characteristic of alkaloids with lycoctonine skeletons: M^+ 451.2567 amu (10%), $C_{24}H_{37}NO_7$ (calcd. 451.2569); 436.2325 (100%), $M^+ - CH_3$ (calcd. 436.2314); 418.2242 (40%), $\{M^+ - CH_3\} - H_2O$ (calcd. 418.2229); 395.2286 (6%), $M^+ - C_3H_4O$ (calcd. 395.2307), ejection of acroleine from ring A owing to the carbimolamine inner ether². The IR (KBr) gave absorptions at 3420 (OH), 1115 and 1090 (C-O), 990 and 890 cm^{-1} (inner ether³). Its PMR ($CDCl_3$) displayed signals at δ 1.10 (3H, t, $J = 7Hz$, $N-CH_2-CH_3$) 3.35 (3H, s, OCH_3), 3.43 (6H, s, two OCH_3), 3.67 (2H, br. s, CH_2OH), 4.00 and 4.08 (1H each, s) which could be assigned to either C-6 α H or C-19H.

These spectroscopic data led to structure I being tentatively assigned to 18-hydroxy-14-O-methylgadesine, assuming the oxygenation pattern of lycoctonine-type alkaloids⁴. To confirm this structure an X-ray analysis was performed. The compound crystallized in the

orthorhombic space group $P2_12_12_1$ with $a = 26.861(3)$, $b = 10.043(2)$, $c = 8433(2)\text{\AA}$, $U = 2274.9\text{\AA}^3$ and four molecules $C_{24}H_{37}NO_7 \cdot H_2O$ per unit cell. The structure was refined to an R of 0.043 for 1772 unique diffractometer data $\{I \geq 3\sigma(I)\}$. The seven-member ring is stabilized in a boat form by a strong intramolecular hydrogen bond between $H(08) \dots O(6) = 1.92\text{\AA}$ and ring A exists as a skew-boat form.



It is interesting to note that 18-hydroxy-14,0-methylgadesine, like gadesine⁶, is another example of a naturally occurring lycoctonine-type alkaloid with C-1-C-9 inner ether. Furthermore we have also isolated delsoline and delcosine⁴, previously reported in this plant⁵ and gigactonine⁷, identified by their $^{13}\text{C-NMR}$ spectra.

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