ANDESINE: AN ALKALOIDAL NAPHTHALENOPYRONE

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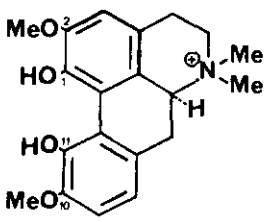
Abstract —Berberis actinacantha and B. darwinii (Berberidaceae) of Chilean origin have furnished the alkaloid andesine (4) which is probably derived biogenetically from (+)-magnoflorine (1) and magnoflorinemethine (2).

As part of a continuing study of the alkaloids of Chilean Berberis actinacantha Mart. ex Schult. and B. darwinii Hook., we have obtained the new amorphous red alkaloid andesine (4), $C_{20}H_{21}NO_6$, ν max $CHCl_3$ 1655, 1680, 3480 cm^{-1}, *which occurs in both plants.*[1]
Andesine exhibits a complex UV spectrum, λ max MeOH 220, 312, 344, 362 nm (log ϵ 4.44, 4.51, 3.85, 3.78) denoting a highly conjugated system. The 200 MHz NMR spectrum in $CDCl_3$ has been summarized around expression 4. An arresting feature of this spectrum is the one-proton singlet at δ 5.99 assigned to the hydrogen of a pyrone system. Two methoxyl singlets were also in evidence, one at δ 3.86 due to a methyl ester, and the other at δ 4.05 representing an aromatic methoxyl. A set of two doublets situated at δ 7.55 and 8.29, J = 8.8 Hz, denoted two adjacent protons in a naphthalene system.
The chemical shift assignments were confirmed by an NMR NOEDS study[2] whose results are outlined around expression 4-NOE. It will be noted in particular that irradiation of the ester methyl group led to a 1.2% enhancement of the pyrone one-proton singlet absorption.
The mass spectrum of the alkaloid showed a small (0.2%) molecular ion peak m/z 371, and a paramount base peak m/z 58 representing the dimethyliminium cation, $CH_2N(CH_3)_2^+$. Other peaks were at m/z 370 (0.6), 313 (0.1), 312 (0.2) and 280 (0.6). The dominating base peak m/z 58 stands as an independent proof for the presence of the dimethylaminoethyl side chain in andesine (4).
Andesine (4) should be viewed within the larger framework of recently characterized novel alkaloids from various Berberis species, all of which appear to originate biogenetically from oxida-



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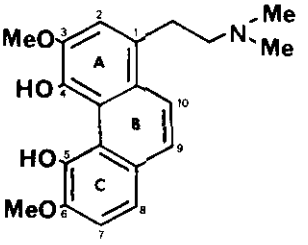

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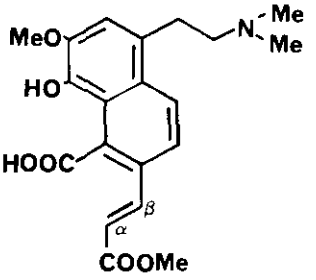

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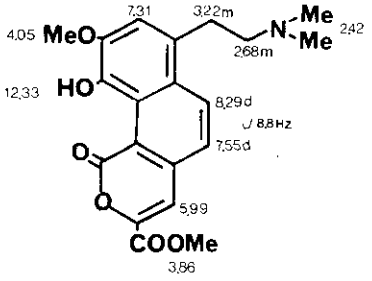

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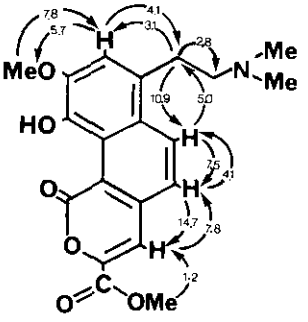
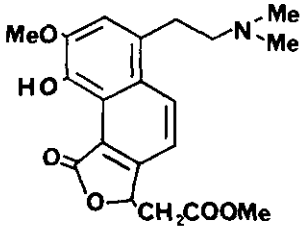


4 - NOE



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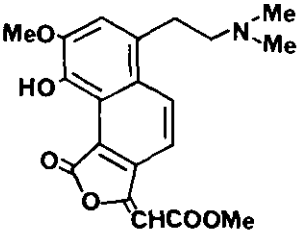

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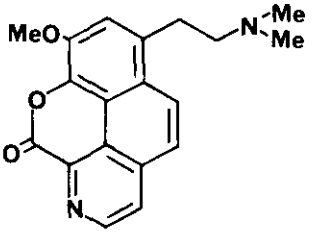

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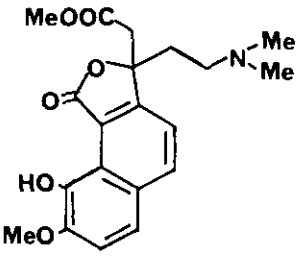

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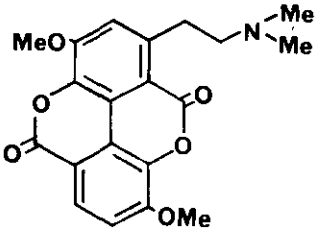

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tion of magnoflorinemethine (2), which is itself formed from the widely occurring 1,2,10,11-tetraoxygenated aporphine (+)-magnoflorine (1).[3]

Thus, intradiol catechol dioxygenase[4] cleavage of ring C of magnoflorinemethine (2) would lead to acid ester 3 which may lactonize in either of two ways. Cyclization at C-α of species 3, followed by oxidation would lead to andesine (4). On the other hand, addition at C-β would provide the yellow chiloenamine (5), which can oxidize to the yellow-orange chiloenine (6).[5]

Alternatively, ring C of the C-5,6 dihydroxy derivative of magnoflorinemethine (2) may undergo distal extradiol cleavage. The resulting aldehydo acid can then lactonize and undergo aminative cyclization to generate the yellow alkaloid santiagonamine (7).[6]

Other relevant alkaloids within this context are aconcaguine (8), which is the result of intradiol cleavage of ring A of magnoflorinemethine (2);[7] and the well known taspine (9)[3] which is formed by oxidation of ring B of species 2.

(+)-Magnoflorine (1) and its Hofmann elimination product magnoflorinemethine (2) must, therefore, function as important channels for the in vivo breakdown of 1,2,10,11-tetraoxygenated aporphines.

ACKNOWLEDGMENT This research was supported by grant CHE-8210699 from the National Science Foundation.

REFERENCES AND FOOTNOTES

1. The dried, powdered plants were defatted with petroleum ether. Extraction was with cold ethanol. The concentrated extracts were fractionated using 3N HCl and then NH_4OH. The alkaloidal fractions were column chromatographed on silica gel, elution being with $CHCl_3$ and increasing amounts of MeOH. The NMR NOEDS data were acquired on a 360 MHz instrument. B. actinacantha (25 kg, dry stems and twigs) furnished 4 mg of andesine (4), while B. darwinii (18 kg, dry stems) gave 3 mg of 4. Magnoflorine (1) occurs abundantly in B. actinacantha.
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Received, 26th November, 1984