

**(+)-Narcidine, a New Alkaloid
from *Narcissus pseudonarcissus***

Emilia Tojo

J. Nat. Prod., **1991**, 54 (5), 1387-1388 • DOI:
10.1021/np50077a023 • Publication Date (Web): 01 July 2004

Downloaded from <http://pubs.acs.org> on April 4, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/np50077a023> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

Journal of Natural Products is published by the American
Chemical Society, 1155 Sixteenth Street N.W., Washington,
DC 20036

(+)-NARCIDINE, A NEW ALKALOID FROM *NARCISSUS PSEUDONARCISSUS*

EMILIA TOJO

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

ABSTRACT.—The bulbs of *Narcissus pseudonarcissus* produced a new crinine-type alkaloid, (+)-narcidine [**1**].

The alkaloidal constituents of *Narcissus pseudonarcissus* L. (King Alfred dafodil) (Amaryllidaceae) have been studied previously (1). The bulbs were shown to contain crinine, lycorenine, galanthamine, and licoryne-type alkaloids. Although our results are essentially in agreement with those findings, we now report the isolation of a new crinine-type alkaloid, namely (+)-narcidine [**1**].

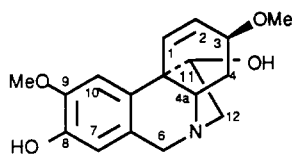
The low resolution mass spectrum of (+)-narcidine [**1**], $C_{17}H_{21}NO_4$, exhibited a typical haemanthamine-type fragmentation pattern (2) with molecular ion m/z 303 (63%) and base peak 229.

The 1H -nmr spectral assignments for

narcidine [**1**] ($CDCl_3/1\% D_2O$) have been indicated in Figure 1. Assignments are based on decoupling as well as on nOe experiments. Noteworthy are the aromatic protons at δ 6.78 and 6.53, the aromatic methoxyl singlet at δ 3.86, and the aliphatic methoxyl singlet at δ 3.35. Two vinylic protons were in evidence at δ 6.48 and 6.35. The quasiaxial (β -oriented) disposition of the C-3 methoxyl was deduced from the coupling constants, $J_{1,3} = 0$ Hz, $J_{2,3} = 5.0$ Hz, $J_{3,4\alpha} = 4.2$ Hz. The assignment of the methoxyl substituent to C-9 was supported by nOe's connecting 9-OMe, H-10 and H-10, H-1.

A significant feature of the nmr spectrum was the long-range W coupling ($J = 1.1$ Hz) between H-11 (δ 3.99) and H-4a (δ 3.38), indicating that the hydroxyl group at C-11 is located as shown in Figure 1.

Comparison of the (+)-narcidine [**1**] nmr data with those of (+)-haemanthamine [**2**] showed the two alkaloids to be structurally similar except for the presence of an aromatic methoxyl singlet



- 1** $R_1 = OMe, R_2 = H$
2 $R_1 = R_2 = OCH_2O$

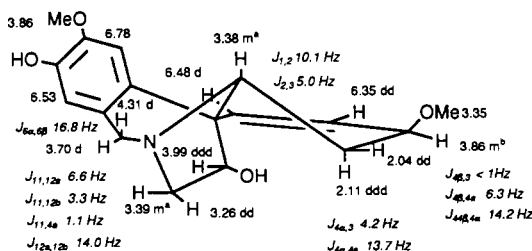


FIGURE 1. 1H -nmr spectral assignments for narcidine [**1**].

^aOverlaps with 3-OMe.

^bOverlaps with 9-OMe.

in the (+)-narcidine [**1**] spectrum instead of the methylenedioxy doublets that appeared in the spectrum of (+)-haemanthamine (**3**).

The similarity between the optical rotation of (+)-narcidine [**1**] ($[\alpha]_D + 16^\circ$) and that of (+)-haemanthamine [**2**] ($[\alpha]_D + 22.7^\circ$) (**4**) suggested the α configuration for the ethano bridge.

In addition to narcidine [**1**], six known alkaloids were also isolated from *N. pseudonarcissus*. These are identified as (+)-haemanthamine (**3**), (+)-hippeastrine (**5**), (-)-galanthamine (**6**), (+)-homolycorine (**7**), (+)-8-*O*-demethylhomolycorine (**7**), and (-)-narcissidine (**8**). The identities were established spectroscopically by comparison with previously reported data. This is the first report of (+)-hippeastrine, (+)-8-*O*-demethylhomolycorine, and (-)-narcissidine having been isolated from *N. pseudonarcissus*.

EXPERIMENTAL

PLANT COLLECTION, EXTRACTION, AND ALKALOID ISOLATION.—The bulbs of *N. pseudonarcissus* (312 g) were collected in State College, Pennsylvania. A bulb specimen was deposited in the Herbarium of the Department of Botany, The Pennsylvania State University. The plant was dried, powdered, and extracted with cold MeOH. The concentrated extract was treated with 5% HCl and filtered. The acid solution was basified with NH_4OH and extracted with CHCl_3 . Solvent evaporation afforded a dark residue (170 mg) that was chromatographed over Si gel using a $\text{CHCl}_3/\text{MeOH}$ gradient for elution. Final purification was by preparative tlc on Si gel glass plates. Nmr spectra were obtained either at 200 or at 360 MHz.

Compounds presently obtained from *N. pseudonarcissus* were: (+)-haemanthamine (456 mg), (+)-hippeastrine (250 mg), (-)-galanthamine

(80 mg), (+)-homolycorine (40 mg), (-)-narcissidine (15 mg), (+)-8-*O*-demethylhomolycorine (5 mg), and (+)-narcidine (3 mg).

(+)-NARCIDINE [1**].**— $[\alpha]_D + 16^\circ$ ($c = 0.11$, MeOH); uv λ max (MeOH) 231, 292 nm ($\log \epsilon$ 3.35, 3.31); ir ν max (CHCl_3) 3350 cm^{-1} ; low resolution eims m/z $[\text{M}]^+$ 303 (63), 274 (38), 272 (32), 271 (56), 259 (61), 229 (100), 213 (39), 181 (92); hreims m/z found 303.1478, calcd 303.1470. Significant $^1\text{H-nmr}$ nOe's are H-10 to 9-MeO, 10%; 9-MeO to H-10, 2%; H-10 to H-1, 19%; H-1 to H-10, 16%; H-2 to H-3, 4%.

ACKNOWLEDGMENTS

The author is grateful to Prof. Maurice Shamma of The Pennsylvania State University for extending laboratory facilities and for useful discussions, and also to the Fulbright Committee for a fellowship. The technical assistance of Mr. Joseph T. Marakovits was very valuable.

LITERATURE CITED

1. H.M. Fales, L.D. Giuffrida, and W.C. Wildman, *J. Am. Chem. Soc.*, **78**, 4145 (1956).
2. A.M. Duffield, R.T. Aplin, H. Budzikiewicz, C. Djerassi, C.F. Murphy, and W.C. Wildman, *J. Am. Chem. Soc.*, **87**, 4902 (1965).
3. V. Pabuççuoğlu, P. Richomme, T. Gözler, B. Kivcak, A.J. Freyer, and M. Shamma, *J. Nat. Prod.*, **52**, 785 (1989).
4. S. Kobayashi, H. Ishikawa, M. Kihara, T. Shingu, and T. Hashimoto, *Chem. Pharm. Bull.*, **25**, 2244 (1977).
5. P.W. Jeffs, A. Abou-Donia, and D. Campau, *J. Org. Chem.*, **50**, 1732 (1985).
6. S. Kobayashi, M. Kihara, K. Yuasa, Y. Imakura, T. Shingu, A. Kato, and T. Hashimoto, *Chem. Pharm. Bull.*, **33**, 5258 (1985).
7. J. Bastida, J.M. Llabrés, F. Viladomat, C. Codina, M. Rubiralta, and M. Feliz, *J. Nat. Prod.*, **50**, 199 (1987).
8. T.H. Kinstle, W.C. Wildman, and C.L. Brown, *Tetrahedron Lett.*, **39**, 4659 (1966).

Received 24 July 1990