Phytochemistry, 1969, Vol. 8, pp. 1745 to 1748. Pergamon Press. Printed in England

SHORT COMMUNICATION

OCCURRENCE OF NON-BASIC METABOLITES IN AMARYLLIDACEAE

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(*Received* 19 *March* 1969)

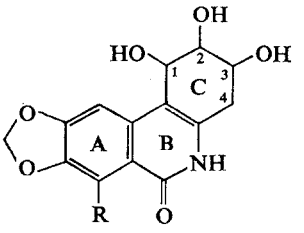
Abstract—Narciclasine and margetine, previously extracted from many species of the genus *Narcissus*, are also present in the genera *Galanthus*, *Haemanthus*, *Leucojum*, *Pancratium*, *Sprekelia*, *Sternbergia* and *Vallota*. In the genus *Hymenocallis* only margetine was detected, but not narciclasine. Both products are absent in the genera *Amaryllis*, *Clivia*, *Crinum* and *Nerine*.

RECENTLY we proposed the structures (I) for narciclasine[1] and (II) for margetine,[2] extracted from fresh bulbs of daffodils. These products could be identical with lycoricidinol and lycoricidine, extracted from fresh bulbs of *Lycoris radiata* Herb., for which the structures (III) and (IV) have been proposed.[3] For margetine,[2] we had no conclusive evidence for a 1, 2, 3 sequence of the hydroxy groups rather than for a 2, 3, 4 sequence: the first structure was preferred by analogy with the structure of narciclasine. In the latter compound, the 1, 2, 3 sequence had been assumed because HIO_4 oxidation of *O*-methyl-narciclasine yielded narciclasic aldehyde,[1] which seemed to support structure (I) better than (III).

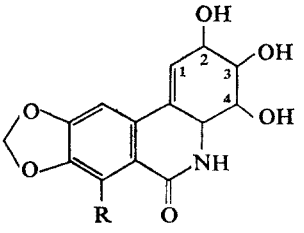
We wish now to report the widespread occurrence of these non-basic metabolites in many other genera and species of Amaryllidaceae.

It is known[4] that the family Amaryllidaceae is formed by four sub-families: Amaryllidoideae (fifty-five genera), Agavoideae (seven genera), Hypoxidoideae (twenty-two genera), Campynematoideae (two genera). About thirty genera, all belonging to the sub-family Amaryllidoideae, have been studied from a chemical point of view for alkaloids.[5] Our preliminary screening has been also directed to this sub-family.

[1] F. PIOZZI, C. FUGANTI, R. MONDELLI and G. CERIOTTI, *Tetrahedron* **24**, 1119 (1968).
[2] C. FUGANTI, A. SELVA and F. PIOZZI, *Chim & Ind.* (*Milano*) **49**, 1196 (1967).
[3] T. OKAMOTO, Y. TORII and Y. ISOGAI, *Chem. Pharm. Bull.* (*Tokyo*) **16**, 1860 (1968).
[4] F. PAX and K. HOFFMANN, in *Die Natürlichen Pflanzenfamilien* (edited by K. HOFFMANN), Vol. 15, Engelmann, Leipzig (1930).
[5] W. C. WILDMAN, in *The Alkaloids* (edited by R. H. F. MANSKE), Vol. 6, pp. 289–413, and Vol. 11, pp. 307–405, Academic Press, New York (1960 and 1968).



(I) R=OH
(II) R=H



(III) R=OH
(IV) R=H

TABLE 1. THE OCCURRENCE OF NARCICLASINE IN NARCISSUS

Species	Variety	Source*	Narciclasine (mg/kg)
N. pseudonarcissus L.	King Alfred	a	85
	Flower Carpet	a	60
	Rembrandt	a	50
	Mount Hood	a	60
	President Lebrun	a	60
	Golden Harvest	a	50
N. incomparabilis Mill.	Tunis	a	80
	Helios	a	200
	Sempre Avanti	a	80
	Mercato	a	85
	Walt Disney	a	60
	Mrs. R. O. Backhouse	a	70
	Scarlet Elegance	a	80
	Carabiniere	a	70
	Oranje Bruid	a	50
N. triandrus L.	Thalia	a	70
	Tresamble	a	60
N. jonquilla L.	Trevithian	a	85
N. poeticus L.	Actaea	a	120
	Cheerfulness	a	50
N. tazetta L.	tipica	b	65
	Geranium	a	85
N. cyclamineus DC.	tipica	a	30
N. odorus L.	rugulosus	a	60
N. canaliculatus Guss.	tipica	a	30
N. serotinus L.	tipica	b	40
N. hybr.	Texas	a	120
	Verger	a	70
	Totus Albus	a	50
	Celebrity	a	85
	Clamor	a	70
	Carlton	a	100

* No serious attempt has been made to divide the highly hybridized *Narcissus* genus into species: the present tabulation is quite tentative from a taxonomic point of view.

Narciclasine and margetine are present in all the thirty-two species and varieties of the genus *Narcissus* which have been examined (Table 1): the narciclasine content varies from 30 to 200 mg/kg of fresh bulbs, while margetine is present in a quite minor quantity, about 2–3 mg/kg. Small amounts of narciprimine[1] were also isolated, while traces of two probable homologues of narciclasine, namely narcicryptine and narcisline, were observed.[2] The narciclasine content may vary during the year: in bulbs of *Narcissus incomparabilis* Mill. var. Helios we have found 200 mg/kg in March at the flowering stage, but only 100–120 mg/kg in November.

The occurrence of such non-basic metabolites has been also investigated in other genera of the family Amaryllidaceae. Variable amounts of narciclasine (Table 2) and traces of margetine are present in *Galanthus* (*G. nivalis* L. and *G. elwesii* Hook), *Haemanthus* (*H. puniceus* L.), *Leucojum* (*L. aestivum* L. var. *pulchellum* Salisb. and *L. vernum* L.), *Pancratium* (*P. maritimum* L.), *Sprekelia* (*S. formosissima* L. Herb.), *Sternbergia* (*S. lutea* L. Ker-Gawl)

TABLE 2. OCCURRENCE OF NARCICLASINE IN THE AMARYLLIDACEAE

Species	Source*	Narciclasine (mg/kg)
Galanthus nivalis L.	a	10
G. elwesii Hook	a	25
Haemanthus puniceus L.	c	< 5
Leucojum aestivum L. var. *pulchellum* (Salisb.)	d	30
L. vernum L.	a	50
Pancratium maritimum L.	b	50
Sprekelia formosisssima (L.) Herb.	a	> 5
Sternbergia lutea (L.) Ker-Gawl	b	< 5
Vallota speciosa L'Her.	a	< 5
Hymenocallis hybr. var. Advance	a	—

(a) Commercially available from Stassen, The Netherlands.
(b) Wild, collected in western Sicily.
(c) Cultivated in the Botanical Garden, University of Parma (Italy).
(d) Cultivated in the Botanical Garden, University of Palermo (Italy).

and *Vallota* (*V. speciosa* L'Her.). In the genus *Hymenocallis* (*H.* hybr. var. Advance), on the other hand, margetine, but not narciclasine, has been identified.

The paper of Okamoto[3] indicates the probable presence of narciclasine and margetine in nearly equal amount (about 100–150 mg/kg ?) in the genus *Lycoris* (*L. radiata* Herb.).

Negative results have been obtained for the genera *Amaryllis* (*A. belladonna* L. and *A. formosissima* L.), *Clivia* (*C. miniata* Regel), *Crinum* (*C. giganteum* Andr., *C. longifolium* Roxb. and *C. pedunculatum* R. Br.) and *Nerine* (*N. bowdenii* W. Watson, *N. crispa* Hort. and *N.* hybr. var. Pink Triumph). In these last genera neither narciclasine nor margetine nor other non-basic metabolites have been detected.

It should be noted that the genera containing alkaloids with three oxygen functions at ring A usually lack narciclasine and vice versa, those genera containing narciclasine or margetine do not yield alkaloids with such three oxygen functions. Moreover, narciclasine is present in genera that also contain some alkaloids with the (+)-crinane skeleton (haemanthamine, haemanthidine), but not in genera like *Crinum*, *Nerine* and *Amaryllis* that yield mainly alkaloids with the (−)-crinane skeleton. The only exceptions we know are *Haemanthus*

albomaculatus Baker (albomaculine[6]), *Pancratium longiflorum* Roxb. (norneronine[7]) and *Hymenocallis americana* Roem. (nerinine[8]): these genera have been found to contain narciclasine or margetine, while the alkaloids present have three oxygen functions on ring A but do not have the crinane skeleton.

EXPERIMENTAL

The extraction of fresh bulbs of the species examined was performed as previously described.[1] Narciclasine was purified from AcOH or from methylcellosolve-water or from water; margetine was isolated from *Narcissus* as the triacetylderivative,[2] while in the other genera it was identified by TLC. In the case of *Haemanthus*, *Sprekelia*, *Sternbergia* and *Vallota*, narciclasine was also detected by TLC and confirmed by preparative TLC and u.v. examination of the fraction corresponding to the R_f value of narciclasine. TLC: on Merck silica gel G, eluent AcOEt, EtOH, H_2O (10:2:1): narciclasine $R_f = 0{\cdot}55$, margetine $R_f = 0{\cdot}46$.

[6] C. K. BRIGGS, P. F. HIGHET, R. J. HIGHET and W. C. WILDMAN, *J. Am. Chem. Soc.* **78**, 2899 (1956).
[7] S. RANGASWAMI and R. V. K. RAO, *Tetrahedron Letters* 4881 (1966).
[8] D. T. BAILEY, Thesis, Iowa State University, Ames, Iowa (1967).