# (-)-3-O-Acetylnarcissidine, a New Alkaloid from Hippeastrum puniceum

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# (−)-3-*O*-ACETYLNARCISSIDINE, A NEW ALKALOID FROM *HIPPEASTRUM PUNICEUM*

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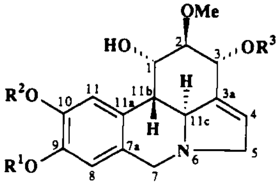
ABSTRACT.—The new alkaloid **1**, (−)-3-*O*-acetylnarcissidine, has been isolated from *Hippeastrum puniceum*. It has been characterized on the basis of spectral data and by comparison with 3-*O*-acetylungiminorine [**3**].

In the course of our research on Caribbean Amaryllidaceae, we studied the alkaloids of *Hippeastrum puniceum* (Lam.) Urb., which is called "duende" in the Dominican Republic. From the dried bulbs, the alkaloids were extracted by a routine acid-base workup procedure (see Experimental). Flash-chromatography eluted three alkaloids: vittatine (1), 11-hydroxyvittatine (1), and a new alkaloid, (−)-3-*O*-acetylnarcissidine [**1**].

Alkaloid **1**, $C_{20}H_{25}NO_6$ from hrms, [α]D −46° ($c=0.5$, $CHCl_3$), obtained as an amorphous solid after cc, was purified by tlc. Its ir spectrum showed absorption due to a carbonyl group at 1735 $cm^{-1}$ and a hydroxyl group at 3400 $cm^{-1}$. The ms spectrum exhibited a molecular peak at *m/z* 375 with characteristic fragment ions at *m/z* 374, 315, 284, and 266, suggesting the presence of hydroxyl, methoxy, and carbomethoxy groups. The $^1$H-nmr spectrum showed two singlet aromatic signals (δ 6.97 and δ 6.78), two deshielded protons (δ 5.96 and δ 5.78), three methoxy signals of which two were on an aromatic ring (δ 3.93 and d 3.89) and one was bound to an aliphatic carbon (δ 3.54), and an acetyl methyl signal (δ 2.06).

On the $^{13}$C-nmr spectrum, a carbonyl peak (δ = 169.3 ppm), five quaternary and three tertiary aromatic or olefinic carbon peaks, five sp$^3$ methines, two methylenes, and four methyl peaks, but no quaternary aliphatic carbons, were identified.

These spectral data are consistent with a narcissidine [**2**] type alkaloid already found in this plant family (2), in which one of the hydroxyl groups is acetylated. The location of the acetyl on the hydroxyl at C-3 was inferred from comparison of nmr data of 3-*O*-acetylungiminorine [**3**] (3) and ungiminorine [**4**] (4,5). Finally, the relative configuration of the new alkaloid **1** was shown to be identical to that of alkaloids **2**, **3**, and **4** by examination of $^1$H- and $^{13}$C-nmr spectra (Tables 1 and 2). Noteworthy is the long range W coupling of 1.0 Hz between H-1 (δ 4.75) and H-3 (δ 5.77), indicating a cis stereochemistry for these protons. As observed for (−)-ungiminorine [**4**] (5), the 5.9 Hz homoallylic coupling between H-11c (δ 3.90) and H-5α (δ 3.67) is diagnostic of C-3a,



**1** $R^1=R^2=Me$, $R^3=Ac$
**2** $R^1=R^2=Me$, $R^3=H$
**3** $R^1=R^2=CH_2$, $R^3=Ac$
**4** $R^1=R^2=CH_2$, $R^3=H$

TABLE 1. $^1$H nmr (250 MHz) of 3-*O*-Acetylnarcissidine [**1**], 3-*O*-Acetylungiminorine [**3**], and Ungiminorine [**4**] [chemical shifts are in ppm (δ) from TMS, coupling constants (*J*) are in Hz].

| Proton | Compound | | |
|---|---|---|---|
| | **1** | **3**[a] | **4**[b] |
| H-1 | 4.75 td, $J$ = 2.1 and 1.0 | 4.62 br s | 4.67 ddd, $J$ = 3.3, 1.2 and 1.0 |
| H-2 | 3.74 dd, $J$ = 2.1 and 1.9 | | 3.65 dd, $J$ = 3.3 and 2.6 |
| H-3 | 5.77 dd, $J$ = 1.9 and 1.0 | 5.89 br s | 4.35 dd, $J$ = 2.6 and 1.2 |
| H-4 | 5.97 dd, $J$ = 2.1 and 1.6 | 5.71 br s | 5.69 dd, $J$ = 2.1 and 2.0 |
| $H_2$-5 | 4.14 ddd, $J$ = 14.8, 2.9 and 1.6 | | 4.04 ddd, $J$ = 14.7, 2.6 and 2.1 |
| | 3.67 ddd, $J$ = 14.8, 5.9 and 2.1 | | 3.56 ddd, $J$ = 14.7, 5.6 and 2.0 |
| $H_2$-7 | 4.16 d, $J$ = 12.9 | 4.04 d, $J$ = 13.0 | 4.07 d, $J$ = 13.0 |
| | 3.72 d, $J$ = 12.9 | 3.62 d, $J$ = 13.0 | 3.62 d, $J$ = 13.0 |
| H-8 | 6.78 s | 6.68 s | 6.75 s |
| H-11 | 6.97 s | 6.90 s | 6.97 s |
| H-11b | 2.88 dd, $J$ = 11.3 and 2.1 | 2.77 m, $J$ = 11.0 | 2.72 dd, $J$ = 11.2 and 1.0 |
| H-11c | 3.90 m | | 3.88 m, $J$ = 11.2, 5.6 and 2.6 |
| 2Ar-OMe | 3.93 and 3.89 s | | |
| C-2 OMe | 3.54 s | 3.47 s | 3.38 s |
| Ac | 2.06 s | 1.99 s | |

[a] Data for this compound are taken from Kobayashi *et al.* (3).
[b] Data for this compound are taken from Richomme *et al.* (5).

C-4 unsaturation and a trans relationship between H-11b and H-11c. All the data were consistent with the proposed structure for the alkaloid **1** which we have called 3-*O*-acetylnarcissidine.

TABLE 2. $^{13}$C nmr (62.53 MHz) of 3-*O*-Acetylnarcissidine [**1**] and Ungiminorine [**4**] [chemical shifts are in ppm (δ) TMS].

| Carbon | **1** | **4**[a] |
|---|---|---|
| C-1 | 68.6[b] | 68.1 |
| C-2 | 80.5 | 80.3 |
| C-3 | 69.0[b] | 68.4 |
| C-3a | 135.5 | |
| C-4 | 126.7 | 127.2 |
| C-5 | 62.1 | 62.3 |
| C-7 | 54.8 | 54.6 |
| C-7a | 129.2 | |
| C-8 | 111.2[c] | 107.8[b] |
| C-9 | 148.4[d] | |
| C-10 | 147.6[d] | |
| C-11 | 108.0[c] | 105.6[b] |
| C-11a | 129.2 | |
| C-11b | 41.4 | 41.5 |
| C-11c | 62.5 | 63.4 |
| 2Ar-OMe | 56.3 | |
| C-2 OMe | 58.5 | 58.1 |
| CO*Me* | 21.2 | |
| *C*OMe | 169.3 | |

[a] Data for this compound are taken from Suau *et al.* (4).
[b–d] Values in the same column with the same superscript may be interchanged.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.— $^1$H nmr and $^{13}$C nmr were recorded on a Brüker WP-250 (250 MHz) instrument in $CDCl_3$ and referenced to TMS (δ 0.0). Low and high resolution ei (70 eV) mass spectra were recorded on a Kratos MS-80. Ir spectra were taken on an Infracord Perkin-Elmer.

PLANT COLLECTION AND EXTRACTION.— *H. puniceum* was collected in February 1990, in the Dominican Republic. A sample, N° 49/1990 Jiménez, was deposited in the herbarium of the Botanical Garden Dr. R.M. Moscoso, Santo Domingo, Dominican Republic. The dried bulb material (720 g) was basified ($NH_4OH$ 2%) and then extracted at room temperature ($CH_2Cl_2$). The solution was treated with dilute HCl (at pH 3). The aqueous phase was then basified with aqueous $NH_4OH$ (at pH 10) and extracted again with $CH_2Cl_2$ to furnish an alkaloid fraction (280 mg) which was submitted to Si gel column flash chromatography [EtOAc-MeOH-$H_2O$-$NH_4OH$ (100:17:13:0.5)] and purified by tlc, affording three alkaloids: vittatine (5 mg), 11-hydroxyvittatine (7 mg), and (−)-3-*O*-acetylnarcissidine [**1**] (7 mg).

3-*O*-ACETYLNARCISSIDINE [**1**].—[α]D −46° ($c$ = 0.5, $CHCl_3$), eims $m/z$ (rel. int. %) $[M]^+$ 375 (3), 374 (8), 314 (19), 315 (59), 301 (7), 298

(10), 285 (31), 284 (100), 266 (56), 228 (20), 162 (9); hrms ($C_{20}H_{25}NO_6$) found 375.1660, calcd 375.1680; ir $\nu$ max ($CHCl_3$) 3400, 1735, 1610, 1515 $cm^{-1}$; $^1H$ nmr see Table 1; $^{13}C$ nmr see Table 2.

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