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ERYTHRINAN ALKALOID FROM *ERYTHRINA* × *BIDWILLII*

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Key Word Index—*Erythrina x bidwillii*; Leguminosae; flowers; alkaloids; erythbidin B.

Abstract—A new alkaloid, erythbidin B, was isolated from flowers of *Erythrina* × *bidwillii*, together with the three known alkaloids, erythraline, erysodine and erythrinine. Their structures were elucidated on the basis of spectroscopic evidence.

INTRODUCTION

As part of our ongoing study on the chemical constituents of the genus *Erythrina*, we have reported [1] the isolation and structural determination of an isoflavan, erythbidin A, from the wood of *Erythrina x bidwillii*, which is widely distributed in subtropical and tropical regions. From the flowers of this species, known erythrinan alkaloids and erythristemine-N-oxide have been isolated earlier [2] and our further investigation of the flowers has now led to the isolation of a novel erythrinan alkaloid, named erythbidin B (**1**), along with three known erythrinan alkaloids (erythraline (**3**) [3, 4], erysodine (**4**) [3, 4] and erythrinine (**5**) [4, 5]). The three known alkaloids had been isolated previously from the leaves [4].

RESULTS AND DISCUSSION

Silica gel chromatography of the alkaloidal fraction of the MeOH extract of flowers afforded a novel erythrinan alkaloid, erythbidin B (**1**), and three known erythrinan alkaloids (**3–5**).

Erythbidin B (**1**) was obtained as an amorphous solid and the molecular formula was confirmed to be $C_{18}H_{17}NO_5$ by HR mass spectrometry (*m/z* 327.1110). The mass spectrum showed also the $[M]^+$ at *m/z* 327 with 100% relative abundance and significant fragments at *m/z* 312 $[M-Me]^+$, 296 $[M-OMe]^+$ and 294 $[M-H-MeOH]^+$, indicating an erythrinan alkaloid with a 1, 6-diene system [6, 7]. In the ^1H NMR spectrum also, the characteristic dienoid proton signals (δ 5.76, 5.99 and 6.63) were observed [8]. The IR spectrum exhibited the presence of hydroxyl (3450 cm^{-1}) and carbonyl (1670 cm^{-1}) groups. Further support for the existence of the hydroxyl group in **1** was provided by the formation of a monoacetate (**2**). The ^1H NMR spectrum revealed signals of a methylenedioxy group (δ 5.94 and 5.98), three aliphatic protons in the A ring (δ 1.95, 2.60 and 3.72), two aliphatic protons in the B ring (δ 4.37 and 4.43), a methoxyl group (δ 3.30) and two aromatic protons (δ 6.88 and 7.22), the latter being a low-field proton ascribed to H-17 because of the carbonyl group at the C-11 position. In addition, a carbinolic proton signal at the C-10 position (δ 5.26) appeared as a singlet and the assignment was determined from the HMBC spectrum, which revealed correlations between H-10 and C-12 (δ 129.6) and C-11 (δ 172.8). The unambiguous assignment of all the ^1H NMR and ^{13}C NMR signals of **1** was accomplished by ^1H-^1H COSY, HMQC and HMBC spectra. The stereochemistry of the hydroxyl group at the C-10 position was determined from the NOESY spectrum (Fig. 1), which displayed NOE interaction between H-10 and H-4e (δ 2.60), showing that the carbinolic proton at the C-10 position and the equatorial proton at C-4 has a cis-relationship. The configuration of the hydroxyl group was thus equatorial. As erythrinan alkaloids with a 3-methoxy substituent have the 3R-configuration [7], the absolute stereochemistry at the C-10 position was R. Therefore, the structure was represented as formula **1**. This is the first example of a C-10 oxygenated erythrinan alkaloid.

EXPERIMENTAL

General

MPs: uncorr. CC: Merck silica gel 60 (230–400 mesh). TLC: Kieselgel 60 F_{254} (Merck), spots vis-

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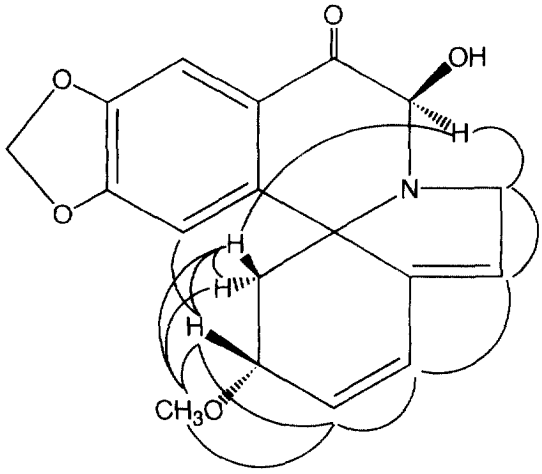

Fig. 1. NOE interactions observed in the phase-sensitive NOESY spectrum of **1**.

ualized by fluorescence at 254 nm or by spraying with Dragendorff's reagent. ^{1}H NMR (400 and 600 MHz) and ^{13}C NMR (67.5) spectra were measured in $CDCl_3$ (TMS int. standard). UV: MeOH. IR: $CHCl_3$.

Plant material

Flowers of *E. x bidwillii* were collected at Kagoshima Prefecture, Japan, in June, 1996. A voucher specimen is deposited at the Department of Natural Product Chemistry in the Faculty of Pharmacy, University of Meijo.

Extraction and isolation

Flowers (148 g) were extracted with MeOH and the solvent evapd to give a dark green residue. The residue was suspended in 5% HCl and washed with Et_2O. The HCl soln was made alkaline with NH_4OH and extracted with CH_2Cl_2. The CH_2Cl_2 soln was dried (Na_2SO_4) and evapd to leave a brownish residue. This was chromatographed on silica gel and eluted with $CHCl_3$–MeOH (40:1, 20:1 and 10:1) to afford **3** (40 mg), **4** (25 mg), **5** (133 mg) and **1** (110 mg), which was further purified by CC [benzene-EtOAc (10:1) and (1:1)]. The known compounds (**3**–**5**) were identified by direct comparison with authentic samples, isolated previously from leaves of *E. x bidwillii* [4].

Erythbidin B (1). Amorphous solid. $[\alpha]_D$ +148° (MeOH, c 0.1). CD (MeOH; c 3.06×10^{-5}): $\Delta\varepsilon$ +2.26 (286), +4.40 (252), −9.16 (218). IR ν_{max} cm^{-1}: 3450, 1670, 1650. UV λ_{max} nm (log ε): 205 (4.52), 243 (4.04), 291 (3.54). EIMS *m/z* (rel. int.): 327 ([M]$^+$, 100), 312 (23), 296 (74), 294 (34), 284 (6), 278 (13), 270 (7), 268 (12), 266 (14), 250 (5), 240 (7), 238 (7), 227 (6.5), 181 (6.7), 165 (8), 149 (10). HRMS *m/z* 327.1110: (M$^+$, calcd for $C_{18}H_{17}NO_5$: 327.1106). ^{1}H NMR ($CDCl_3$): δ 1.95 (1H, *t*, *J* = 11.0 Hz, H-4a), 2.60 (1H, *dd*, *J* = 11.0, 5.1 Hz, H-4e), 3.30 (3H, *s*, OMe), 3.72 (1H, *m*, H-3), 4.05 (1H, *br s*, OH), 4.37 (1H, *dd*, *J* = 17.6, 2.2 Hz, H-8), 4.43 (1H, *d*, *J* = 17.6 Hz, H-8), 5.26 (1H, *s*, H-10), 5.76 (1H, *br s*, H-7), 5.94 (1H, *d*, *J* = 1.5 Hz, OCH_2O), 5.98 (1H, *d*, *J* = 1.5 Hz, OCH_2O), 5.99 (1H, *d*, *J* = 10.3 Hz, H-2), 6.63 (1H, *dd*, *J* = 10.3, 2.2 Hz, H-1), 6.88 (1H, *s*, H-14), 7.22 (1H, *s*, H-17). ^{13}C NMR ($CDCl_3$): δ 172.8 (C-11), 147.4 (C-15), 146.7 (C-16), 138.6 (C-6), 131.6 (C-2), 131.2 (C-13), 129.6 (C-12), 124.1 (C-1), 119.9 (C-7), 106.1 (C-17), 103.9 (C-14), 101.4 (OCH_2O), 76.1 (C-3), 71.7 (C-5), 67.7 (C-10), 56.4 (OMe), 54.1 (C-8), 39.5 (C-4).

Acetylation of erythbidin B (1). A mixt. of **1** (17 mg), Ac_2O (0.5 ml) and pyridine (0.5 ml) was stirred overnight at room temp. After work-up, the reaction residue was purified by chromatography on silica gel using $CHCl_3$ to yield at acetate **2** (8 mg) as a viscous oil. $[\alpha]_D$ +154° (MeOH, c 0.1). IR ν_{max} cm^{-1}: 1750, 1680. UV λ_{max} nm (log ε): 204 (4.50), 242 (4.00), 290 (3.53). EIMS *m/z* (rel. int.): 369 ([M]$^+$, 54), 354 (3), 338 (23), 326 (100), 312 (20), 296 (49), 294 (13), 278 (6), 268 (5), 266 (12), 250 (3.9), 181 (3.9), 165 (6), 149 (13). HRMS *m/z*: 369.1220 (M$^+$, calcd for $C_{20}H_{19}NO_6$: 369.1211). ^{1}H NMR ($CDCl_3$): δ 1.99 (1H, *t*, *J* = 11.2 Hz, H-4a), 2.38 (3H, *s*, $COCH_3$), 2.66 (1H, *dd*, *J* = 11.2, 4.4 Hz, H-4e), 3.30 (3H, *s*, OMe), 3.69 (1H, *m*, H-3), 4.33 (1H, *dd*, *J* = 17.1, 1.0 Hz, H-8), 4.40 (1H, *d*, *J* = 17.1 Hz, H-8), 5.77 (1H, *br s*, H-7), 5.96 (1H, *d*, *J* = 1.5 Hz, OCH_2O), 5.97 (1H, *d*, *J* = 10.3 Hz, H-2), 5.99 (1H, *d*, *J* = 1.5 Hz, OCH_2O), 6.43 (1H, *s*, H-14), 6.63 (1H, *dd*, *J* = 10.3, 2.0 Hz, H-1), 6.93 (1H, *s*, H-17), 6.95 (1H, *d*, *J* = 1.0 Hz, H-10).

1: R = H

2: R = Ac

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