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AN ISOFLAVAN FROM *ERYTHRINA X BIDWILLII*

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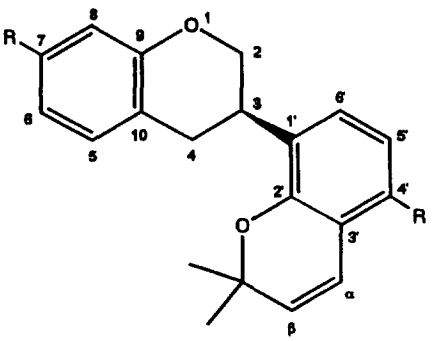
Key Word Index—*Erythrina x bidwillii*; Leguminosae; isoflavan; erythbidin A; pterocarpan.

Abstract—A new isoflavan, erythbidin A, was isolated from the wood of *Erythrina x bidwillii*, together with three known isoflavans, phaseollinisoflavan, 2′-methoxyphaseollinisoflavan, and 2′-*O*-methylphaseollidinisoflavan and another pterocarpan, sandwicensin. Erythbidin A has a dimethylpyrene substitution at the 2′,3′-position.

INTRODUCTION

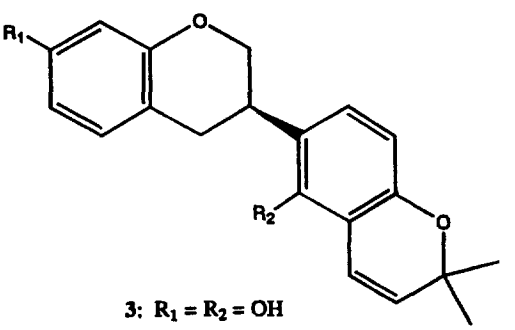
In a continuation of our study on the non-alkaloidal compounds of genus *Erythrina*, we have reported [1] the isolation and characterization of three new pterocarpans, erystagallins A–C, from the wood of *Erythrina crista-galli*. We have carried out a study of the non-alkaloidal components of *Erythrina x bidwillii*, distributed in the subtropical and tropical regions, from which phenolic constituents [2, 3] have been reported from the root bark. We now describe the isolation and structure elucidation of a new isoflavan, named erythbidin A (**1**), along with three previously known isoflavans (phaseollinisoflavan (**3**) [4, 5], 2′-methoxyphaseollinisoflavan (**5**) [6] and 2′-*O*-methylphaseollidinisoflavan (**6**) [7]) and known pterocarpan, sandwicensin (**7**) [8], from the wood of *E. x bidwillii*.



1: R = OH
2: R = OMe

RESULTS AND DISCUSSION

Silica gel chromatography of the *n*-hexane and the methylene chloride extract of the wood of *E. x bidwillii* gave the novel isoflavan, erythbidin A (**1**), together with four known compounds (**3** and **5**–**7**). Erythbidin A (**1**) was obtained as a colourless oil and the molecular formula was confirmed to be $C_{20}H_{20}O_4$ by the HRMS (324.1373). The IR and UV spectral data were closely similar to those of **3**. The mass spectrum of **1** showed an intense M^+-15 peak (*m/z* 309) resulting from the molecule ion by expulsion of methyl group of dimethylchromene ring and prominent *retro* Diels–Alder peaks were also observed at *m/z* 202 and 187,



3: R_1 = R_2 = OH
4: R_1 = R_2 = OMe
5: R_1 = OH, R_2 = OMe

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as reported for other isoflavans [9]. The ^{1}H NMR spectrum revealed characteristic signals of the chromene ring (δ 1.42, 1.43, 5.66 and 6.70), the aliphatic protons of the C_2-C_4 portion of the isoflavan moiety (δ 2.77, 2.94, 3.42, 3.97 and 4.19), a set of *ortho*-aromatic protons (δ 6.40 and 6.87) and an ABX system aromatic protons (δ 6.29, 6.37 and 6.89) (Table 1). The location of two hydroxyl groups was confirmed by the DIFNOE experiment of the dimethyl ether (**2**) which displayed NOE interactions between the methoxyl group at C-4′ position (δ 3.80) and the aromatic proton at C-5′ position (δ 6.39), and/or the α-olefinic proton (δ 6.67) and between the methoxyl group at C-7 position (δ 3.77) and the aromatic proton at C-6 position (δ 6.48) and/or the aromatic proton at C-8 position (δ 6.43) (Fig. 1). The absolute stereochemistry at C-3 was assigned to be *R*-configuration from its positive CD of **1** [10, 11].

Compound (**3**) is the known isoflavan, phaseollinisoflavan [4, 5] and there have not been found any unequivocal discrimination between spectra (IR, UV, MS, ^{1}H NMR, ^{13}C NMR (Table 2)) of these two compounds (**1** and **3**). The hydroxyl group at the C-2′ position was confirmed by the DIFNOE technique of the dimethyl ether (**4**) which exhibited NOE interactions between the methoxyl group at C-2′ position (δ 3.76) and the methine proton at the C-3 (δ 3.52), and/or the α-proton (δ 6.59) (Fig. 2).

Compound (**5**) is 2′-methoxyphaseollinisoflavan, earlier isolated from the diseased bean of *Phaseolus vulgaris* [6] in whose NOESY spectrum NOE interactions were observed between the methoxyl group at C-2′ position (δ 3.76) and the methine proton at the C-3 (δ 3.51), and/or the α-proton (δ 6.58) and the absolute stereochemistry at C-3 position was *R*-configuration (positive CD). The ^{13}C NMR spectrum is reported here for the first time. Assignment of all the ^{1}H NMR and ^{13}C NMR signals of **1**, **3** and **5** was accomplished by analyses of the ^{1}H–^{1}H COSY, HMQC and HMBC spectra.

EXPERIMENTAL

General

Mps: uncorr. CC: Merck silica gel 60 (230–400 mesh). TLC: Kieselgel 60 F_{254} (Merck); spots were detected by spraying with 50% H_2SO_4 and by UV light. ^{1}H NMR (400 and 600 MHz) and ^{13}C NMR (67.5 MHz): TMS int. standard. UV: MeOH. IR: $CHCl_3$.

Plant material

Wood of *E. x bidwillii* were collected at Kagoshima prefecture, Japan, in July 1995.

Extraction and isolation

Wood of *E. x bidwillii* (3.05 kg) was extracted with MeOH and evaporated to give a residue. The residue was divided into *n*-hexane-, CH_2Cl_2-, and EtOAc-soluble fractions. The *n*-hexane-soluble fraction (5.9 g) was chromatographed on silica gel and eluted with *n*-hexane–benzene (1 : 1), benzene, benzene–EtOAc (10 : 1) and benzene–EtOAc (1 : 1); 20 ml fractions were collected. Frs 86–133 were separated by repeated CC [benzene–EtOAc (10 : 1)] to give **5** (33 mg) and **7** (11 mg). The CH_2Cl_2-soluble fraction (7.8 g) was chromatographed on silica gel and eluted with benzene, benzene–EtOAc (10 : 1) and benzene–EtOAc (1 : 1); 20 ml fractions were collected. Frs 73–88 were purified by CC [$CHCl_3$–Me_2CO (40 : 1)] to afford **6** (124 mg). Frs 89–103 were separated by CC [*n*-hexane–Me_2CO (4 : 1) and (1 : 1)] to provide **3** (37 mg) and **1** (123 mg) which was further purified by CC [*n*-hexane–Me_2CO (1 : 1)]. The identification of **6** and **7** was made by comparison of the physical and spectral data with those published in the literature [7, 8].

2′-Methoxyphaseollinisoflavan (**5**)

Colourless oil. $[\alpha]_D$ +18° (MeOH, *c* 0.1). CD (MeOH; $c\ 3.37\times10^{-5}$): $\Delta\varepsilon$ +1.46 (289), ±0 (240), −0.77 (231). IR ν_{max} cm^{-1}: 3600, 1625, 1610. UV λ_{max} nm: 227, 270, 279, 290 (sh), 312. MS *m/z*: 338 [M]$^+$, 323 (100%), 307, 293, 286, 243, 239, 216, 201, 185. HRMS *m/z*: 338.1508 (M$^+$, calcd for $C_{21}H_{22}O_4$: 338.1517). Spectral data were identical to those reported for 2′-methoxyphaseollinisoflavan [6]. ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Erythbidin A (**1**)

Colourless oil. $[\alpha]_D$ −13° (MeOH, *c* 0.1). CD (MeOH; $c\ 2.69\times10^{-5}$): $\Delta\varepsilon$ +1.97 (289), ±0 (241), −4.57 (233). IR ν_{max} cm^{-1}: 3600, 1625, 1600. UV λ_{max} nm: 225, 280, 310 (sh). MS *m/z*: 324 [M]$^+$, 309 (100%), 239, 202, 187. HRMS *m/z*: 324.1373 (M$^+$, calcd for $C_{20}H_{20}O_4$: 324.1360). ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Methylation of Erythbidin A

A mixture of **1** (18 mg) and trimethylsilyldiazomethane (2.0 M solution in *n*-hexane) (1.5 ml) in MeOH (2 ml) was kept overnight at room temperature. After the excess of trimethylsilyldiazomethane was decomposed with a solution of AcOH–MeOH (5 : 1), the solvent was removed. The resulting residue was purified by chromatography on silica gel using CH_2Cl_2 to yield **2** (8.9 mg, 46%) as a colourless oil. IR ν_{max} cm^{-1}: 1620, 1600, 1590. UV λ_{max} nm: 226, 280, 289, 312. MS *m/z*: 352 [M]$^+$, 337 (100%), 216, 201, 189, 186. HRMS *m/z*: 352.1670 (M$^+$, calcd for $C_{22}H_{24}O_4$: 352.1673). ^{1}H NMR: Table 1.

Phaseollinisoflavan (**3**)

Colourless oil. $[\alpha]_D$ −9° (MeOH, *c* 0.1). CD (MeOH; $c\ 3.14\times10^{-5}$): $\Delta\varepsilon$ +1.40 (302), ±0 (241),

Table 1. ^{1}H NMR spectral data of **1–5**

H	**1***	**2†**	**3***	**4†**	**5†**
2	3.97 *t*-like (10.3)	4.04 *t*-like (10.3)	3.95 *t*-like (10.3)	3.96 *t*-like (10.3)	3.94 *t*-like (10.3)
	4.19 *ddd* (10.3, 3.4, 2.2)	4.31 *ddd* (10.3, 5.2, 1.5)	4.21 *ddd* (10.3, 3.4, 2.1)	4.28 *ddd* (10.3, 5.2, 1.5)	4.27 *ddd* (10.3, 3.7, 1.5)
3	3.42 *m*	3.53 *m*	3.48 *m*	3.52 *m*	3.51 *m*
4	2.77 *dd* (15.4, 5.2)	2.86 *dd* (15.4, 5.2)	2.79 *dd* (15.4, 5.2)	2.87 *dd* (15.4, 5.2)	2.85 *dd* (15.4, 5.2)
	2.94 *dd* (15.4, 11.0)	3.00 *dd* (15.4, 11.0)	2.92 *dd* (15.4, 11.0)	2.92 *dd* (15.4, 11.0)	2.90 *dd* (15.4, 11.0)
5	6.89 *d* (8.2)	6.99 *d* (8.2)	6.89 *d* (8.2)	6.98 *d* (8.2)	6.93 *d* (8.2)
6	6.37 *dd* (8.2, 2.2)	6.48 *dd* (8.2, 2.2)	6.37 *dd* (8.2, 2.2)	6.48 *dd* (8.2, 2.2)	6.39 *dd* (8.2, 2.2)
8	6.29 *d* (2.2)	6.43 *d* (2.2)	6.28 *d* (2.2)	6.44 *d* (2.2)	6.37 *d* (2.2)
5′	6.40 *d* (8.8)	6.39 *d* (8.8)	6.33 *d* (8.8)	6.59 *d* (8.8)	6.59 *d* (8.8)
6′	6.87 *d* (8.8)	6.90 *d* (8.8)	6.92 *d* (8.8)	6.87 *d* (8.8)	6.87 *d* (8.8)
α	6.70 *d* (10.3)	6.67 *d* (10.3)	6.79 *d* (10.3)	6.59 *d* (9.5)	6.58 *d* (10.3)
β	5.66 *d* (10.3)	5.58 *d* (10.3)	5.69 *d* (10.3)	5.66 *d* (9.5)	5.66 *d* (10.3)
Me	1.42 *s*	1.41 *s*	1.38 *s*	1.43 *s*	1.43 *s*
Me	1.43 *s*	1.42 *s*	1.38 *s*	1.43 *s*	1.43 *s*
7-OR	8.07 *s*	3.77 *s*	8.33 *brs*	3.78 *s*	4.94 *brs*
2′-OR			8.09 *brs*	3.76 *s*	3.76 *s*
4′-OR	8.39 *s*	3.80 *s*			

* $(CD_3)_2CO$.
† $CDCl_3$.

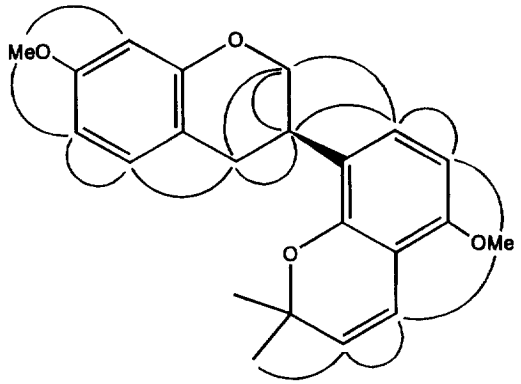

Fig. 1. NOE interactions of compound **2** in PSNOESY and DIFNOE specta.

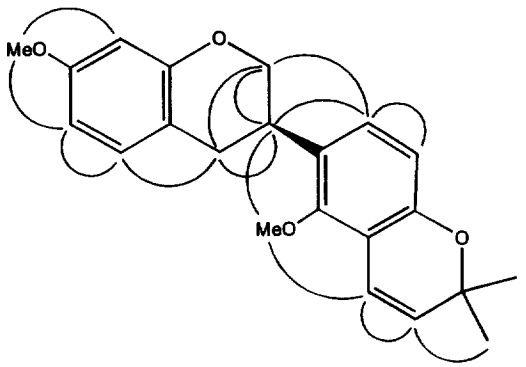

Fig. 2. NOE interactions of compound **4** in PSNOESY and DIFNOE specta.

−3.48 (231). IR ν_{max} cm^{-1}: 3600, 1625, 1600. UV λ_{max} nm: 227, 280, 310 (sh). MS *m/z*: 324 $[M]^+$, 309 (100%), 239, 202, 187. HRMS *m/z*: 324.1350 (M^+, calcd for $C_{20}H_{20}O_4$: 324.1360). ^1H NMR: Table 1; ^{13}C NMR: Table 2. Structure of **3** was confirmed by the DIFNOE spectrum and spectral data was the same as those reported for phaseollinisoflavan [4, 5].

Methylation of phaseollinisoflavan

A mixture of **3** (16 mg) and trimethylsilyldiazomethane (2.0 M solution in *n*-hexane) (1.5 ml) in MeOH (2 ml) was treated by a procedure similar to that described for **2**, giving **4** (8 mg, 46%) as a colourless oil. IR ν_{max} cm^{-1}: 1620, 1600, 1590. UV λ_{max} nm: 227, 270 (sh), 279, 289, 312. MS *m/z*: 352 $[M]^+$, 337 (100%), 216, 201, 189, 186. HRMS *m/z*: 352.1692 (M^+, calcd for $C_{22}H_{24}O_4$: 352.1673). ^1H NMR: Table 1.

Table 2. ^{13}C NMR spectral data of **1**, **3** and **5**

C	1*	3*	5†
2	70.5	70.5	70.6
3	32.5	32.3	31.2
4	31.1	31.4	31.7
5	131.0	131.0	130.4
6	108.7	108.7	107.9
7	157.5	157.5	154.9
8	103.7	103.6	103.2
9	156.0	155.9	155.0
10	114.3	114.2	114.7
1′	120.8	121.7	126.0
2′	152.1	151.0	154.3
3′	110.3	111.1	114.9
4′	152.7	153.3	152.8
5′	108.3	109.4	112.7
6′	127.8	127.7	126.9
α	118.0	117.7	117.2
β	129.2	130.1	130.7
Me_2C	76.4	75.8	75.8
Me	27.8	27.8	27.8
Me	27.9	27.8	27.8
OMe			62.7

* $(CD_3)_2CO$.
† $CDCl_3$.

REFERENCES

1. Tanaka, H., Tanaka, T. and Etoh, H., *Phytochemistry*, 1997, **45**, 835.
2. Iinuma, M., Tanaka, T., Mizuno, M., Yamamoto, H., Kobayashi, Y. and Yonemori, S., *Chemical and Pharmaceutical Bulletin*, 1992, **40**, 2749.
3. Iinuma, M., Okawa, Y., Tanaka, T., Kobayashi, Y. and Miyauchi, K.-I., *Heterocycles*, 1994, **39**, 687.
4. Burden, R. S., Bailey, J. A. and Dawson, G. W., *Tetrahedron Letters*, 1972, 4175.
5. Seifert, K., Härtling, S., Porzel, A., Johne, S. and Krauss, G., *Zeitschrift für Naturforschung*, 1993, **48c**, 550.
6. VanEtten, H. D., *Phytochemistry*, 1973, **12**, 1791.
7. Preston, N. W., *Phytochemistry*, 1975, **14**, 1131.
8. Mitscher, L. A., Gollapudi, S. R., Gerlach, D. C., Drake, S. D., Véliz, E. A. and Ward, J. A., *Phytochemistry*, 1988, **27**, 381.
9. Pelter, A., Stainton, P. and Barber, M., *Journal of Heterocyclic Chemistry*, 1965, **2**, 262.
10. Wong, E., in *The Flavonoids*, ed. J. B. Harborne, T. J. Mabry and H. Mabry, Chapman and Hall, London, 1975, p. 776.
11. Kurosawa, K., Ollis, W. D., Redman, B. T., Sutherland, I. O., Alves, H. M. and Gottlieb, O. R., *Phytochemistry*, 1978, **17**, 1423.