Erythrinan Alkaloids from Seeds of *Erythrina velutina*

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Four new Erythrinan alkaloids (1—4) were isolated from the seeds of *Erythrina velutina*. The structures of these new compounds 1—4 were elucidated by spectroscopic methods including 2D-NMR. Three of four were found to be novel sulfated Erythrinan alkaloids.

Key words Erythrinan alkaloid; *Erythrina velutina*; Leguminosae

In the course of our search for biologically and structurally unique compounds from medicinal plants in tropical and subtropical regions,[1)] we have continued to investigate the constituents of *Erythrina* species. The genus *Erythrina* (Leguminosae) consists of more than a hundred species of trees, shrubs and herbaceous plants that are widely distributed throughout tropical and warm regions of the world.[2)] *Erythrina velutina* WILLD. is commonly called Mulungu in Brazil, and its bark is used as a remedy for insomnia, convulsion, nervous cough and rheumatism in the north of Brazil.[3)] Phytochemical analyses have demonstrated that *Erythrina* plants accumulate Erythrinan alkaloids,[4,5)] benzylisoquinoline alkaloids,[6)] isoflavonoids[7)] and pretocarpanes.[8)] The Erythrinan alkaloids are characterized by their unique tetracyclic spiro-amine framework. Therefore, their structures with various biological properties have recently attracted attention as a synthetic target.[9,10)] In previous papers, we described the isolation and structural characterization of an indole derivative, hypaphorine, and its sleep-inducing effect on normal mice,[11)] as well as the isolation and structural characterization of a new Erythrinan alkaloid, erysodine *N*-oxide, together with known compounds, and the evaluation of the isolated compounds in terms of the enhanced activity for tumor necrosis factor (TNF)-related apoptosis-inducing ligand (TRAIL).[12)] In this paper, we describe the isolation and structural elucidation of four new Erythrinan alkaloids (**1**—**4**), including novel sulfated alkaloids from the high polarity portion extracted with *n*-BuOH, of the seeds of *Erythrina velutina*. The new constituents isolated from *E. velutina* were elucidated by spectroscopic methods, including ^{1}H- and ^{13}C-NMR, high resolution (HR)-MS and comparison with data in the literature.

Results and Discussion

The seeds of *E. velutina* were crushed and then extracted with MeOH and 80% MeOH. These MeOH-soluble materials were successively partitioned between petroleum ether, EtOAc and 3% tartaric acid. Each water-soluble material was adjusted to pH 10 with Na_2CO_3 and then partitioned between $CHCl_3$ and *n*-BuOH to obtain alkaloidal portions. The *n*-BuOH-soluble materials were subjected to amino-silica-gel and silica-gel column chromatography. The obtained fractions were further purified using a silica-gel column and silica-gel HPLC to afford four new compounds **1**—**4** and a known compound, hypaphorine.

Compound **1** {$[\alpha]_D^{23}$ +126 (c=0.18, MeOH)} was obtained as a brown amorphous solid. Its molecular formula was determined as $C_{18}H_{21}NNaO_6S$ by HR-FAB (+) MS [m/z 402.0986 $(M+H)^+$, $\Delta -0.1$ mmu] and the IR spectrum implied the presence of an aromatic moiety and a conjugate olefin (1615, 1510, 1459 cm^{-1}). Furthermore, **1** showed strong IR absorptions at 1262 and 1046 cm^{-1}, suggesting the presence of a sulfate group. The UV spectrum showed λ_{max} (MeOH) at 226 (log ε 4.20) and 277 (log ε 3.39) nm. The gross structure of **1** was deduced from detailed analysis of the ^{1}H- and ^{13}C-NMR-aided 2D-NMR experiments (^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond connectivity (HMBC)), which indicated the presence of four methylenes, one sp^3 quaternary carbon, one sp^3 oxy-methine, three sp^2 methines, one sp^2 quaternary carbon, two aromatic methine carbons, two aromatic quaternary carbons, two aromatic oxy-quaternary carbons and two methoxy groups. With two double bonds and an aromatic ring accounting for six of nine unsaturations, it was concluded that **1** contains four rings including one aromatic ring. The ^{1}H–^{1}H COSY spectrum revealed connectivities of C-1 to C-4, C-7 to C-8, and C-10 to C-11 (Fig. 1). The HMBC correlations (Fig. 1) were observed: H-17/C-11, C-12, C-13 and C-15, H-14/C-5 (δ_C 69.4: a spiro-carbon), C-12, C-13 and C-16, H-11/C-10, C-12, C-13 and C-17, H-10/C-5, C-8, C-11 and C-12, H-8/C-5, C-6, C-7 and C-10, H-7/C-1, C-5, C-6 and C-8, H-1/C-3, C-5, C-6 and C-7, H-2/C-4 and C-6, H-3/C-1, C-2, C-4 and C-

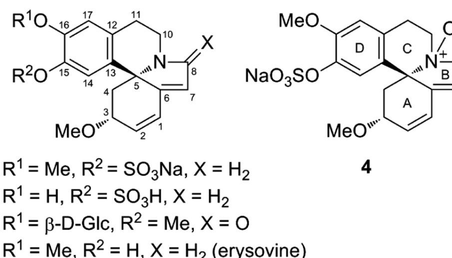

Chart 1. Structures of Compounds **1**—**5**

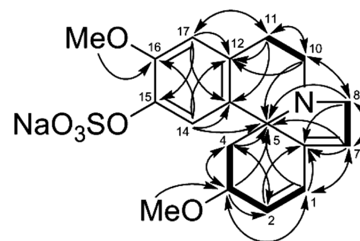

Fig. 1. ^{1}H–^{1}H COSY (—) and HMBC (→) Correlations of **1**

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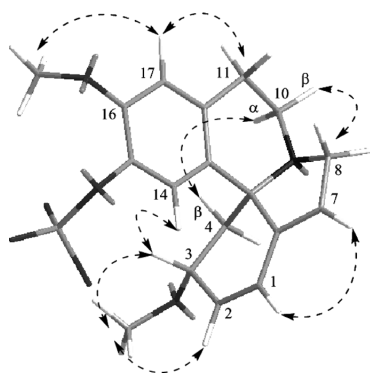

Fig. 2. NOESY Correlations of **1**

5, and H-4/C-2, C-3 and C-5. These correlations showed that **1** was a typical Erythrinan alkaloid having a characteristic spiro-carbon positioned in the center of rings of A, B and C with two olefins of $\Delta^{1,2}$ (δ_H 6.53 dd, δ_C 125.2, C-1; δ_H 6.05 br d, δ_C 134.0, C-2) and $\Delta^{6,7}$ (δ_C 142.9, C-6; δ_H 5.73 br s, δ_C 122.0, C-7). Two methoxy groups were attached to C-3 and C-16 as deduced from the HMBC correlations of 3-OMe (δ_H 3.34 s) and 16-OMe (δ_H 3.81 s) to methoxy-bearing carbons C-3 (δ_C 77.0) and C-16 (δ_C 152.4), respectively. On the other hand, in ^{13}C-NMR, the aromatic methine carbon of C-14 exhibited a markedly downfield shift by 8.8 ppm in comparison with that of erysovine (**5**).[13] These facts indicated that a sodium sulfate group was located at C-15. The nuclear Overhauser effect spectroscopy (NOESY) correlations (Fig. 2) of 16-OMe/H-17 suggested that the methoxy group was located at C-16. Another methoxy group located at C-3 in α-orientation was deduced from the NOESY cross-peaks of 3-OMe/H-3 and H-3/H-14. Other NOESY correlations of H-17/H$_2$-11, H$_2$-8/H-10β, H-4β/H-10α and H-1/H-7 were satisfied with the relative stereochemistry of the new compound **1** as depicted. Furthermore, the circular dichroism (CD) spectrum of **1** showed a Cotton effect at λ_{max} (MeOH) 231 nm ($\Delta\varepsilon$ +23.3), which suggested that the absolute configuration of the 3-methoxy group was *R*.[14] Compound **1** was converted into erysovine (**5**) by acid hydrolysis.

Compound **2** {$[\alpha]_D^{23}$ +90 (c=0.31, MeOH)} was obtained as a colorless amorphous solid. Its molecular formula was determined as $C_{17}H_{20}NO_6S$ by HR-FAB (+) MS [*m/z* 366.1016 (M+H)$^+$, Δ +0.4 mmu] and the IR spectrum implied the presence of a hydroxyl group (3437 cm^{-1}), an aromatic moiety and a conjugate olefin (1623, 1509, 1453 cm^{-1}). Additionally, **2** showed strong IR absorptions at 1269 and 1046 cm^{-1} (a sulfate group). The 1D- and 2D-NMR (^{1}H–^{1}H COSY, HSQC and HMBC) spectra of **2** were similar to those of **1**, except for the absence of a methoxy group at C-16. Furthermore, these data indicated that a sulfate ester group was located at C-15. The relative configuration was determined to be the same as **1** deduced from the NOESY spectrum of **2**. Thus, compound **2** was assigned as erysopine 15-*O*-sulfate.

Compound **3** {$[\alpha]_D^{23}$ +86 (c=0.093, MeOH)} was obtained as a colorless amorphous solid. Its molecular formula was determined as $C_{24}H_{30}NO_9$ by HR-FAB (+) MS [*m/z* 476.1924 (M+H)$^+$, Δ +0.4 mmu]. The IR spectrum implied the presence of hydroxyl groups (3402 cm^{-1}) and a carbonyl group (1651 cm^{-1}). The 1D-NMR spectra and 2D-NMR correlations showed that **3** was a typical Erythrinan alkaloid having a characteristic spiro-carbon (δ_C 68.7, C-5) in the center of rings, with two olefins of $\Delta^{1,2}$ and $\Delta^{6,7}$ in A and B rings, respectively (Tables 1, 2). Furthermore, the presence of a carbonyl group in unsaturated γ-lactam ring (ring B) was suggested from the HMBC cross-peaks of H-10 to C-8 (carbonyl, δ_C 173.3) and H-7 (δ_H 6.04 s) to C-8 (Tables 1, 2). In addition, there were two methoxy groups attached to C-3 and C-15, as deduced from HMBC correlations of 3-OMe and

Table 1. ^{1}H-NMR Data of Compounds **1**—**5** (in CD_3OD)

Position	**1** δ_H mult. (J)	**2** δ_H mult. (J)	**3** δ_H mult. (J)	**4** δ_H mult. (J)	**5**[15] δ_H mult. (J)
1	6.53 dd (10.2, 2.1)	6.61 dd (10.2, 2.1)	7.00 dd (10.2, 2.3)	6.64 dd (10.2, 2.1)	6.56 dd (10.2, 2.2)
2	6.05 br d (10.2)	6.19 br d (10.2)	6.43 br d (10.2)	6.20 br d (10.2)	6.02 br d (10.2)
3	4.21 m	4.15 m	3.80 m	4.32 m	4.03 m
4	1.75 t (11.4)	1.92 t (11.3)	1.62 t (11.6)	2.88 t (11.4)	1.76 t (11.4)
	2.51 dd (11.4, 5.7)	2.71 dd (11.3, 5.6)	2.94 dd (11.6, 4.8)	2.16 dd (11.4, 5.8)	2.51 dd (11.4, 5.6)
7	5.73 br s	5.86 br s	6.04 s	5.79 br s	5.75 br s
8	3.59 br s, 2H	3.93 br d (15.0)		3.98 dd (15.3, 3.3)	3.61 dd (14.5, 3.3)
		4.03 dd (15.0, 2.9)		4.59 br d (15.3)	3.52 br d (14.3)
10	3.05 m	3.33 m	3.67 m	3.68 m, 2H	3.44 m
	3.45 m	3.76 ddd (13.2, 9.0, 6.2)	3.82 m		2.92 m
11	2.71 m	3.01 dt (17.4, 6.2)	3.20 dt (16.1, 7.1)	3.13 m, 2H	2.96 m
	3.02 m	3.09 ddd (17.4, 9.0, 6.2)	3.01 ddd (16.1, 7.1, 4.4)		2.69 m
14	7.40 s	7.25 s	6.87 s	7.36 s	6.72 s
17	6.80 s	6.79 s	7.12 s	6.85 s	6.71 s
1′			4.90 d (7.3)		
2′			3.47 t (7.3)		
3′			3.47 m		
4′			3.36 m		
5′			3.43 m		
6′			3.66 m		
			3.88 dd (12.1, 2.2)		
OMe-3	3.24 s	3.35 s	3.34 s	3.38 s	3.33 s
OMe-15			3.75 s		
OMe-16	3.70 s			3.82 s	3.82 s

Table 2. ^{13}C-NMR Data of Compounds **1**—**5** (in CD_3OD)

Position	**1** δ_C	**2** δ_C	**3** δ_C	**4** δ_C	**5**[15] δ_C
1	125.2	124.5	124.8	125.8	126.0
2	134.0	135.1	138.7	135.0	132.9
3	77.0	76.6	76.3	77.0	77.6
4	40.9	39.9	42.4	32.9	41.8
5	69.4	71.4	68.7	83.9	68.1
6	142.9	142.2	160.4	139.7	143.9
7	122.0	120.6	119.9	118.8	123.1
8	56.9	57.7	173.3	71.7	57.3
10	43.9	44.5	39.0	59.8	44.6
11	24.3	22.8	27.6	27.8	24.7
12	131.1	130.5	128.5	128.8	126.0
13	129.2	125.8	131.7	128.4	131.6
14	121.7	121.7	110.3	121.6	112.9
15	141.3	140.4	148.9	141.9	145.7
16	152.4	150.7	147.8	153.1	148.1
17	114.2	118.2	118.9	113.4	113.9
1′			102.6		
2′			74.9		
3′			77.9		
4′			71.4		
5′			78.4		
6′			62.6		
OMe-3	56.9	57.0	56.9	56.8	56.6
OMe-15			56.9		
OMe-16	56.7			56.6	56.3

15-OMe, to each methoxy-bearing carbon, respectively (Fig. 3). Furthermore, analysis of the ^{1}H- and ^{13}C-NMR data and HSQC spectrum of **3** indicated five oxygenated sp^3 methines and one sp^3 oxygenated methylene in addition to its Erythrinan alkaloid. The sequences of ^{1}H–^{1}H COSY from C-1′ to C-6′, and those of ^{1}H- and ^{13}C-NMR chemical shifts, suggested the presence of a glucose moiety. Furthermore, the cross-peak of an anomeric proton signal at δ_H 4.90 (d, J=7.3 Hz, H-1′) to C-16 (δ_C 147.8) and the NOESY cross-peaks of H-1′/H-17 suggested that a β-glucose unit was located at C-16 (Fig. 3). The NOESY correlations of H-15-OMe/H-14, H-3/H-14, H-3-OMe/H-3 and H-3-OMe/H-4β revealed that the methoxy groups were located at C-3 and C-15, and H-3 was in a β-orientation (Fig. 3). Thus, the structure of compound **3** was assigned as 16-*O*-β-D-glucopyranosyl-coccoline.

Compound **4** {$[\alpha]_D^{23}$ +76 (c=0.16, MeOH)} was obtained as a colorless, amorphous solid. Its molecular formula was determined as $C_{18}H_{21}NNaO_7S$ by HR-FAB (+) MS [m/z 418.0939 $(M+H)^+$, Δ +0.3 mmu]. **4** showed strong IR absorptions at 1264 and 1047 cm^{-1}, suggesting the presence of a sulfate group. The ^{1}H- and ^{13}C-NMR spectra of **4** were similar to those of **1**. The ^{1}H–^{1}H COSY and HMBC correlations showed that **4** was a typical Erythrinan alkaloid. Two methoxy groups were attached to C-3 and C-16, as deduced from the HMBC correlations of H-3-OMe and H-16-OMe, to each methoxy-bearing carbon, respectively. Additionally, the molecular formula of **4** indicated the presence of one extra oxygen atom. In ^{13}C-NMR, the spiro-carbon (C-5) and two methylene carbons of C-8 and C-10 exhibited markedly downfield shifts by 14.5, 14.8 and 15.9 ppm in comparison with those of **1**, respectively (Table 2). These facts suggested that the nitrogen atom was oxygenated. The orientation of the oxygen atom of *N*-oxide might be α-facing owing to the

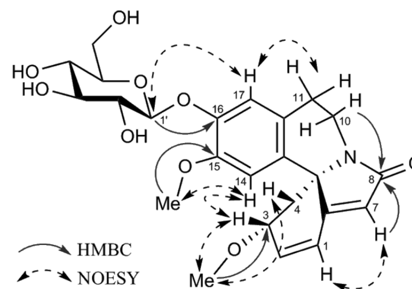

Fig. 3. HMBC and NOESY Correlations of **3**

downfield shifts of H-4α (δ_H 2.88 t) (Table 1). The relative configuration was determined to be the same as that of **1** deduced from its NOESY spectrum. Therefore, compound **4** was assigned as sodium erysovine *N*-oxy-15-*O*-sulfate.

Compounds **1**, **2** and **4** are new Erythrinan alkaloids containing a sulfate group from *Erythrina velutina*. These sulfated compounds are the first reported to be isolated as Erythrinan alkaloids.

Experimental

General Experimental Procedures Optical rotations were measured on a Jasco DIP-370 digital polarimeter. UV spectra were obtained using a Jasco V-560 UV/VIS spectrophotometer. A Perkin Elmer spectrum-100 Fourier transform (FT)-IR spectrometer was used for scanning IR spectroscopy with KBr pellets. 1D- and 2D-NMR spectra were recorded on a Bruker AVANCE-500 spectrometer using tetramethylsilane as the internal standard. Mass spectra were obtained on a JEOL HX-100 spectrometer. Column chromatography was performed using silica gel (Wako-gel C-300, Wako Ltd., Japan) and amino silica gel (Chromatorex NH 100—200 mesh, Fuji Silysia Chemical Ltd., Japan). Fractions were monitored by TLC, and spots were visualized using Dragendorff's reagent.

Plant Material The seeds of *Erythrina velutina* WILLD. (Local name: Mulungu, Leguminosae) were purchased in São Paulo, Brazil, in 2005. The plant was identified by Dr. G. Hashimoto (Centro de Pesquisas de História Natural, São Paulo, Brazil), and a voucher specimen (No. B-160) has been deposited at the Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University.

Extraction and Isolation The seeds of *E. velutina* (954 g) were crushed and then extracted with MeOH (Ext. A, 40.3 g), and then with 80% aqueous MeOH (Ext. B, 24.0 g). The MeOH-soluble materials (Ext. A) were partitioned between petroleum ether (3.78 g), EtOAc (1.01 g) and 3% aqueous tartaric acid. The water-soluble materials were adjusted to pH 10 with Na_2CO_3 and successively partitioned between $CHCl_3$ (2.77 g) and *n*-BuOH (11.29 g). The *n*-BuOH-soluble materials (8.37 g) were separated in a NH-silica gel column ($CHCl_3$–MeOH, 95 : 10→0 : 100, Chromatorex NH 100—200 mesh, Fuji Silysia Chemical Ltd., Japan) to obtain 22 fractions (F1—F22). F10 ($CHCl_3$: MeOH, 6 : 4, 460 mg) was separated using a silica gel column ($CHCl_3$–MeOH, 70 : 30→40 : 60, Wako-gel C-300, Wako Ltd., Japan) to isolate **1** (52.8 mg); F20 ($CHCl_3$: MeOH, 3 : 7, 71.1 mg) was separated using a silica gel column ($CHCl_3$–MeOH, 7 : 3) to give **2** (4.6 mg). On the other hand, the *n*-BuOH-soluble materials (421 mg) were separated using a silica gel column (MeOH–acetone, 99 : 1) to obtain 3 fractions (F2-1—3). The first fraction (F2-1, 272 mg) was chromatographed on a silica gel column ($CHCl_3$–MeOH, 9 : 1) and then HPLC ($CHCl_3$–MeOH, 9 : 1, YMC-Pack SIL, YMC Ltd., Japan) was used to obtain **3** (4.2 mg). Furthermore, the 80% aqueous MeOH (Ext. B) was partitioned using the above method to obtain alkaloidal portions of $CHCl_3$-soluble (439 mg) and *n*-BuOH-soluble (4.86 g) materials. The *n*-BuOH-soluble materials were separated using a NH-silica gel column ($CHCl_3$–MeOH, 95 : 5→0 : 100) to give 11 fractions (F3-1—11). The F3-10 ($CHCl_3$: MeOH, 1 : 1, 519 mg) was further chromatographed on a silica gel column ($CHCl_3$–MeOH, 9 : 1) to isolate **4** (9.9 mg).

Sodium Erysovine 15-*O*-Sulfate (**1**): Brown, amorphous solid; $[\alpha]_D^{23}$ +126 (c=0.18, MeOH); UV (MeOH) λ_{max} (log ε) 226 (4.20), 277 (3.39) nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 231 (+23.3) nm; IR (KBr) ν_{max} 1615, 1516, 1510, 1459, 1454, 1262, 1097, 1049 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; HR-FAB (+) MS m/z 402.0986 $[M+H]^+$ (Calcd for $C_{18}H_{21}NNaO_6S$, 402.0987).

Erysopine 15-*O*-Sulfate (**2**): Colorless, amorphous solid; $[\alpha]_D^{23}$ +90 (c=0.31, MeOH); UV (MeOH) λ_{max} (log ε) 227 (4.27), 277 (3.54) nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 232 (+19.3) nm; IR (KBr) ν_{max} 3437, 1623, 1509, 1453, 1269, 1096, 1046, 837, 761 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; HR-FAB (+) MS m/z 366.1016 $[M+H]^+$ (Calcd for $C_{17}H_{20}NO_6S$, 366.1012).

16-*O*-β-D-Glucopyranosyl Coccoline (**3**): Colorless, amorphous solid; $[\alpha]_D^{23}$ +86 (c=0.093, MeOH); UV (MeOH) λ_{max} (log ε) 223 (4.05), 273 (3.37) nm; IR (KBr) ν_{max} 3402, 1651, 1513, 1455, 1418, 1385, 1327, 1260, 1212, 1077 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; HR-FAB (+) MS m/z 476.1924 $[M+H]^+$ (Calcd for $C_{24}H_{30}NO_9$, 476.1920).

Sodium Erysovine *N*-Oxy-15-*O*-sulfate (**4**): Colorless, amorphous solid; $[\alpha]_D^{23}$ +76 (c=0.16, MeOH); UV (MeOH) λ_{max} (log ε) 228 (4.18), 278 (3.33) nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 235 (+11.5) nm; IR (KBr) ν_{max} 1615, 1516, 1459, 1408, 1264, 1091, 1047, 830 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; HR-FAB (+) MS m/z 418.0939 $[M+H]^+$ (Calcd for $C_{18}H_{21}NNaO_7S$, 418.0936).

Acid Hydrolysis of 1 HCl (1 N, 2 ml) was added to **1** (5 mg) at room temperature and the reaction mixture was stirred at 80 °C for 30 min. The solution was neutralized using 5 N NaOH. The aglycon was extracted with $CHCl_3$ and evaporated under reduced pressure to give compound **5** (1 mg). Compound **5** {$[\alpha]_D^{23}$ +210 (c=0.03, CH_3Cl)} was identified with erysovine using ^{1}H- and ^{13}C-NMR data.[15)]

Acknowledgement We thank Dr. G. Hashimoto (Centro de Pesquisas de História Natural, São Paulo, Brazil) for the identification of *Erythrina velutina*.

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15) The ^{1}H- and ^{13}C-NMR data in CD_3OD (Tables 1 and 2) of erysovine (**5**) isolated by us were assigned with the aid of 2D-NMR.