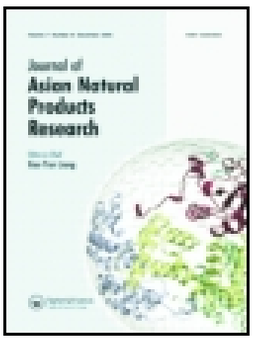

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# Coixlachryside B: a new benzoxazinoid glycoside from the roots of *Coix lachryma-jobi* var. *ma-yuen* (Gramineae)

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**ABSTRACT**

*Coix lachryma-jobi* L. var. *ma-yuen* has been a source of food and traditional folk medicine in some parts of Asia for thousands of years; however, the roots of this plant have not been phytochemically investigated. Herein, we report the isolation of a new benzoxazinoid glycoside, coixlachryside B (**1**), along with ten known compounds (**2–11**), from the roots of *C. lachryma-jobi* var. *ma-yuen* using a variety of chromatographic methods. Among the known compounds, the absolute configuration of compound **4** was determined. The structures of all compounds were elucidated by interpreting NMR spectroscopic data, and experimental and calculated electronic circular dichroism spectra.

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## 1. Introduction

*Coix lachryma-jobi* L. var. *ma-yuen* Stapf. (Gramineae), commonly known as adlay or Job's tears, is a miscellaneous cereal that has been an important food item in some parts of East and Southeast Asia for thousands of years [1]. *Coix* seeds have been used as a traditional folk medicine for relieving heat, inducing diuresis, assisting pus drainage, stimulating lung and spleen function, and treating arthritis and diarrhea [1,2]. *C. lachryma-jobi* var. *ma-yuen* has been reported to have several chemical constituents, including benzoxazinoids, lactams, lignans, phenolic acids, flavonoids, fatty acids, and phytosterols [3–9]. The chemical constituents of *Coix* contribute to its range of medical and nutritional benefits. Some of these compounds have shown a wide range of biological activities, including immunomodulatory, anti-cancer, antioxidant, anti-inflammatory, anti-proliferative, and gastroprotection activities [7–12]. The aim of this study was to phytochemically investigate the roots of *C. lachryma-jobi* var. *ma-yuen*. Herein we report the isolation of a new benzoxazinoid glycoside, (2*R*)-2-*O*-(6-acetyl-*β*-D-glucopyranosyl)-7-methoxy-1,4(2*H*)-benzoxazin-3-one (**1**), as well

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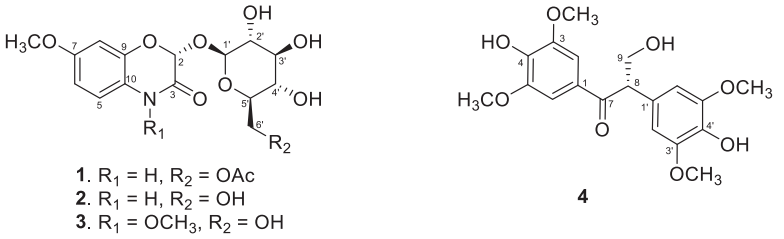


**Figure 1.** Structures of compounds **1–4** isolated from *C. lachryma-jobi* var. *ma-yuen*.

as 10 known compounds (**2**–**11**, Figure 1). Among the 10 known compounds, the absolute stereochemistry of one previously isolated phenolic derivative was identified for the first time in this study.

## 2. Results and discussion

Compound **1** was obtained as a colorless amorphous powder, and its molecular formula was determined to be $C_{17}H_{21}NO_{10}$ by HRESIMS (*m/z* 400.1254 $[M+H]^+$), which requires the molecule to have eight degrees of unsaturation. The $^1H$ and $^{13}C$ NMR data for **1** (Table 1) suggested the presence of one ABX-type aromatic spin system [$\delta_H$ 6.83 (1H, d, $J=9.1$ Hz, H-5), 6.60 (1H, d, $J=2.1$ Hz, H-8), and 6.59 (1H, dd, $J=9.1$, 2.1 Hz, H-6); $\delta_C$ 156.0, 141.6, 120.3, 116.3, 108.8, and 104.4], an aromatic $OCH_3$ group [$\delta_H$ 3.68 (3H, s, 7-$OCH_3$); $\delta_C$ 55.8], an acetoxyl group [$\delta_H$ 2.09 (3H, s, $COOCH_3$); $\delta_C$ 170.8 and 21.2], an acetal methine moiety [$\delta_H$ 5.60 (1H, s, H-2); $\delta_C$ 96.2], and an amine [$\delta_H$ 10.8 (1H, s, NH)]. In addition, the $^1H$ and $^{13}C$ NMR spectra revealed sets of signals corresponding to a $\beta$-glucopyranosyl group [$\delta_H$ 4.62 (1H, d, $J=8.4$ Hz, H-1′); $\delta_C$ 103.7 (C-1′), 73.5 (C-2′), 76.8 (C-3′), 70.1 (C-4′), 74.5 (C-5′), 64.2 (C-6′)] (Table 1). The $^{13}C$ NMR spectrum of **1** was almost superimposable onto that of HMBOA-Glc (**2**) except for the presence of one acetoxyl group. The correlation between H-6′ and $COOCH_3$ observed in the HMBC spectrum of **1** establishes that the acetoxyl moiety was located at C-6′. The free sugar was confirmed to be D-glucose after acid hydrolysis, optical rotation measurement, and TLC comparison with an authentic sample. In addition, the $\beta$-configuration of the sugar moiety was determined from the $^1H$-NMR coupling constant of its anomeric proton ($J_{1,2}>7.0$ Hz) [13], while the C-2 connectivity of the sugar was determined on the basis of HMBC correlations between Glc H-1′ ($\delta_H$ 4.62) and C-2 ($\delta_C$ 96.2) (Figure 2). The absolute configuration of C-2 was confirmed as being 2*R* by the positive optical-rotation $([\alpha]_D^{25}$ +44.5) and the positive Cotton effects ($\Delta\varepsilon$ +14.8) observed at 216 nm in the circular dichroism (CD) spectrum of **1** [3]. Therefore, the structure of compound **1** was determined to be (2*R*)-2-*O*-(6-acetyl-$\beta$-D-glucopyranosyl)-7-methoxy-1,4(2*H*)-benzoxazin-3-one, with the trivial name "coixlachryside B."

Compound **4** was obtained as a white amorphous powder that exhibited a quasi-molecular ion peak at *m/z* 379.13971 $[M+H]^+$ by positive-ion HRESIMS, which corresponds to the molecular formula $C_{19}H_{22}O_8$. The 1- and 2-D NMR data for **4** are in agreement with those of the previously reported tarennone (1,2-bis(3,5-dimethoxy-4-hydroxyphenyl)-3-hydroxy-propan-1-one) isolated from the whole plant of *Tarenna*

**Table 1.** $^{1}$H- and $^{13}$C-NMR spectroscopic data of compounds **1** and **4**.[a]

| **1**[b] | | | **4**[c] | | |
|---|---|---|---|---|---|
| Position | $\delta_H$ mult. (*J* Hz) | $\delta_C$ mult. | Position | $\delta_H$ mult. (*J* Hz) | $\delta_C$ mult. |
| 2 | 5.60 s | 96.2 d | 1 | | 129.0 s |
| 3 | | 160.0 s | 2 | 7.35 s | 107.8 d |
| 5 | 6.83 d (9.1) | 116.3 d | 3 | | 148.9 s |
| 6 | 6.59 dd (9.1, 2.1) | 108.8 d | 4 | | 142.3 s |
| 7 | | 156.0 s | 5 | | 148.9 s |
| 8 | 6.60 d (2.1) | 104.4 d | 6 | 7.35 s | 107.8 d |
| 9 | | 141.6 s | 7 | | 199.4 s |
| 10 | | 120.3 s | 8 | 4.75 dd (8.4, 4.9) | 56.8[d] d |
| 1′ | 4.62 d (8.4) | 103.7 d | 9 | 4.26 dd (10.5, 8.4) | 65.4 t |
| 2′ | 2.91 t (9.1) | 73.5 d | | 3.73 dd (10.5, 4.9) | |
| 3′ | 3.16 t (9.1) | 76.8 d | 1′ | | 129.3 s |
| 4′ | 3.02 t (9.1) | 70.1 d | 2′ | 6.63 s | 106.6 d |
| 5′ | 3.42 m | 74.5 d | 3′ | | 149.6 s |
| 6′ | 4.31 dd (11.9, 2.1) | 64.2 t | 4′ | | 136.0 s |
| | 4.01 dd (11.9, 2.1) | | 5′ | | 149.6 s |
| NH | 10.8 s | | 6′ | 6.63 s | 106.6 d |
| 7-$OCH_3$ | 3.68 s | 55.8 s | 3,5-$OCH_3$ | 3.85 s | 56.8[d] s |
| $COOCH_3$ | | 170.8 s | 3′,5′-$OCH_3$ | 3.80 s | 56.7 s |
| $COOCH_3$ | 2.09 s | 21.2 q | | | |

[a]Peaks were assigned by analyses of the 1D and 2D NMR spectra (Data recorded at 700 and 175 MHz).
[b]Measured in DMSO-$d_6$.
[c]Measured in $CD_3OD$.
[d]Overlapping signals.

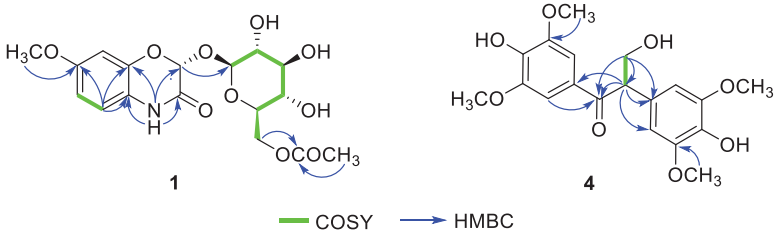


**Figure 2.** Selected COSY and HMBC correlations of compounds **1** and **4**.

*attenuata* [14], but whose absolute stereochemistry was not assigned. Hence, the absolute configuration of **4** was determined by comparing experimental and calculated electronic circular dichroism (ECD) data, which is a method that has been applied for determining the absolute configurations of natural metabolites [15]. Following systematic conformational searching, geometry optimizations, and ECD calculations, the ECD spectrum was generated using the SpecDis 1.64 software. The calculated ECD spectrum of **4** (Figure 3) closely matches the experimental spectrum, which suggests the 8*S* absolute configuration; consequently, **4** was determined to be (8*S*)-tarennone, as shown.

The remaining compounds were determined to be (2*R*)-2-hydroxy-7-methoxy-1,4(2*H*)-benzoxazin-3-one glucoside (HMBOA-Glc, **2**) [3], (2*R*)-2-hydroxy-4,7-dimethoxy-1,4(2*H*)-benzoxazin-3-one glucoside (HDMBOA-Glc, **3**) [16], 8*R*-evofolin B (**5**) [17], 3,4,5-trimethoxybenzyl alcohol (**6**) [18], α-hydroxypropiosyringone (**7**) [19], *β*-hydroxypropiovanillone (**8**) [20], *β*-hydroxypropiosyringone (**9**) [21], 1-*O*-feruloylglycerol (**10**) [22], and 10*Z*,13*Z*-nonadecadienoic acid (**11**) [23]; their chemical

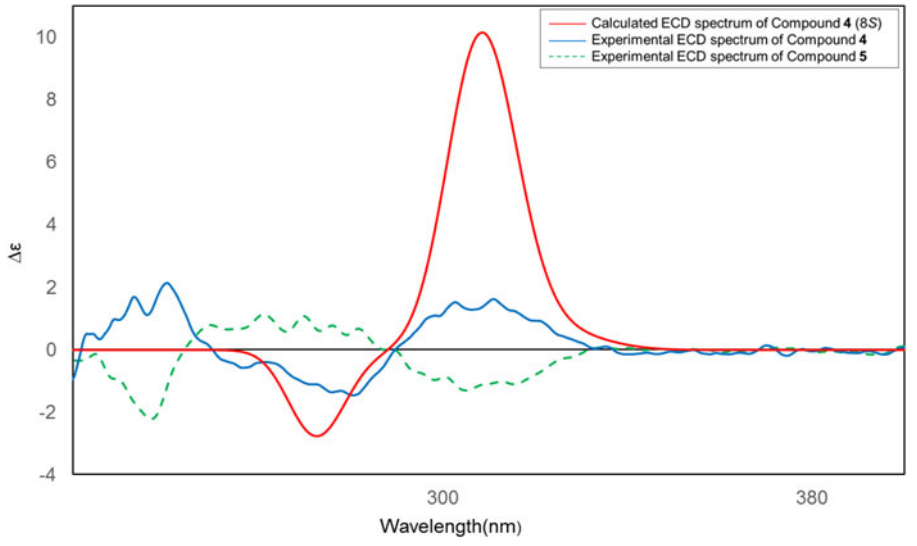


Figure 3. Calculated and experimental ECD spectra of compounds **4** and **5**.

structures were elucidated by comparing their spectroscopic and MS data with those reported in the literature. To the best of our knowledge, compounds **4–11** were isolated for the first time from the *Coix* genus.

## 3. Experimental

### 3.1. General experimental procedures

Optical rotations were measured using a JASCO P-2000 polarimeter, and CD spectra were recorded on a JASCO J-715 spectropolarimeter (Tokyo, Japan). NMR spectra were acquired on a Bruker Ascend III 700 spectrometer (Rheinstetten, Germany) using DMSO-$d_6$ or $CD_3OD$ as solvent. HRESIMS was performed on Triple TOF 5600+ mass spectrometer (AB SCIX, Foster City, CA, USA). Open column chromatography was performed using ODS-A (12 nm S-7 μm, YMC GEL, Kyoto, Japan). Thin-layer chromatography was performed using precoated silica gel 60 F254 (0.25 mm, Merck) plates, and spots were detected using a 10% aqueous vanillin-$H_2SO_4$ spray reagent. Preparative HPLC was performed on a Shimadzu (LC-8A pump and SPD-20A UV/VIS detector) using a YMC-Pack ODS A column (250 × 20 mm I.D.), with a mixed MeCN/$H_2O$ solvent system at a flow rate of 10 ml/min. MPLC (Combi Flash RF, Teledyne ISCO, Lincoln, NE, USA) separations were performed using a Redi*Sep*® Rf silica-gel column. All other chemicals and reagents were of analytical grade.

### 3.2. Plant material

The roots of *Coix lachryma-jobi* var. *ma-yuen* were collected in Yeoncheon-gun, Gyeonggi-do, Korea, in November 2013 and identified by one of the authors (Prof. J. S. Oh). A voucher specimen (G54) was deposited in the herbarium of the Bio-Center, Gyeonggido Business & Science Accelerator, Suwon, Korea.

### 3.3. Extraction and isolation

The dried roots of *C. lachryma-jobi* var. *ma-yuen* (1.9 kg) were extracted with 70% ethanol (2 × 14 L) at room temperature. The combined ethanol extracts were then concentrated *in vacuo* at 40 °C to yield 333.3 g of a residue. The ethanol extract was suspended in distilled water and then partitioned successively with *n*-hexane, $CH_2Cl_2$, EtOAc, and *n*-BuOH, respectively. The EtOAc-soluble layer (5.5 g) was separated using a Diaion HP-20 column chromatography (CC) eluted with a $H_2O$/MeOH (20:80–0:100) step gradient to give seven fractions (G54 − 6−1 to G54 − 6−7). Fraction G54 − 6−3 (1.2 g) was further passed through an RP-18 MPLC column (Redi*Sep*® Rf silica gold 430 g, 150 ml/min) eluted with a $H_2O$/MeCN (95:5–50:50, 50 min) step gradient to give eight fractions (G54 − 7−1 to G54 − 7−8). G54 − 7−4 (120 mg) was purified by preparative HPLC (YMC-Pack ODS-A, 5 μm, 250 × 10 mm I.D., MeCN/$H_2O$, 10:90–20:80, flow rate 12.0 ml/min) to yield compounds **8** ($t_R$ = 14 min, 18.6 mg) and **9** ($t_R$ = 12 min, 2.1 mg). G54 − 7−6 (164 mg) was purified further by preparative HPLC (MeCN/$H_2O$, 15:85 isocratic mode, flow rate 12.0 ml/min) to afford compounds **2** ($t_R$ = 14 min, 39.6 mg), **3** ($t_R$ = 16 min, 6.4 mg), and **7** ($t_R$ = 20 min, 1.0 mg). Subfraction G54 − 7−2 (216 mg) was subjected to reversed-phase $C_{18}$ CC and eluted with MeOH/$H_2O$ (10:90 to 50:50) to obtain eight fractions (G54 − 9−1 to G54 − 9−8). Fraction G54 − 9−2 (65 mg) was purified by preparative HPLC (MeCN/$H_2O$, 15:85 isocratic mode, flow rate 12.0 ml/min) to afford compounds **1** ($t_R$ = 17 min, 7.8 mg) and **6** ($t_R$ = 14 min, 4.0 mg). Fraction G54 − 9−5 (74 mg) was purified further by preparative HPLC (MeCN/$H_2O$, 25:75 isocratic mode, flow rate 12.0 ml/min) to afford compounds **4** ($t_R$ = 10 min, 3.2 mg), **5** ($t_R$ = 17 min, 3.6 mg), and **10** ($t_R$ = 13 min, 4.5 mg). Fraction G54 − 6−5 (1.3 g) was separated by MPLC with a silica-gel column (Redi*Sep*® Rf silica gold 80 g, 85 ml/min) and eluted with a $CHCl_3$/MeOH gradient system (1:0–0:1) to give seven fractions (G54 − 10 − 1 to G54 − 10 − 7). G54 − 10 − 2 (380 mg) was further purified by preparative HPLC (MeOH/$H_2O$, 95:5–100:0, flow rate 8.0 ml/min) to yield compound **11** ($t_R$ = 21 min, 8 mg).

#### 3.3.1. (2R)-2-O-(6-Acetyl-β-D-glucopyranosyl)-7-methoxy-1,4(2H)-benzoxazin-3-one (coixlachryside B, 1)

Colorless amorphous powder; $[\alpha]_D^{25}$ +44.5 (*c* 0.8, MeOH); CD (MeOH) $\Delta\varepsilon_{216\,nm}$ +14.8; $^1$H-NMR (700 MHz, DMSO-$d_6$) and $^{13}$C-NMR (175 MHz, DMSO-$d_6$) spectral data see Table 1; ESIMS: *m/z* 422 $[M + Na]^+$, 369 $[M - H]^-$; HRESIMS (positive mode): *m/z* 400.1245 $[M + H]^+$ (calcd for $C_{17}H_{22}NO_{10}$, 400.1238).

#### 3.3.2. 8S-Tarennone (4)

White amorphous powder; $[\alpha]_D^{25}$ +21.3 (*c* 0.5, MeOH); CD (MeOH) $\Delta\varepsilon_{237\,nm}$ +4.64, $\Delta\varepsilon_{268\,nm}$ −1.97, $\Delta\varepsilon_{311\,nm}$ +2.75; $^1$H-NMR (700 MHz, $CD_3OD$) and $^{13}$C-NMR (175 MHz, $CD_3OD$) spectral data see Table 1; ESI-MS: *m/z* 379 $[M + H]^+$, 401 $[M + Na]^+$, 779 $[2M + Na]^+$, 377 $[M - H]^-$; HRESI-MS (positive ion mode): *m/z* 379.1397 $[M + H]^+$ (calcd for $C_{19}H_{23}O_8$, 379.1387).

### 3.4. Acid hydrolysis of 1, and absolute configuration determination of sugar

A solution of compound **1** (3 mg) in 2M HCl (MeOH/$H_2O$ 4:1, 5 ml) was refluxed at 90 °C for 6 h. After cooling, the reaction mixture was diluted with $H_2O$ (20 ml) and neutralized with $NaHCO_3$, followed by extraction with $CHCl_3$ (3 × 20 ml). The aqueous layer was concentrated to an appropriate volume (1 ml) and examined by TLC (silica gel) ($CHCl_3$/MeOH/$H_2O$ solvent system, 65:35:10) for sugar analysis. The *Rf* value of the D-glucose spot was 0.25, which was detected by spraying with vanillin-sulfuric acid followed by heating. The specific rotation of the free sugar obtained from the aqueous residue was as follow: $[\alpha]_D^{25}$ +47 (c 0.05, $H_2O$) of D-glucose from **1** [24].

### 3.5. Computational methods

Starting with the conformation of compound **4** created by Chem3D modeling, a conformational search was first performed using Chem3D with the MMFF94 force field, and several conformers were selected for further geometry optimization. Geometries were optimized and reoptimized at the B3LYP/6–31 + G(d,p) level using the Gaussian 09 software package. TDDFT CD calculations were performed at the CAM–B3LYP/SVP level on the optimized conformers using a CPCM solvent model in methanol. The calculated CD spectra were simulated and generated with a half-bandwidth of 0.3 eV using SpecDis 1.64 software [25]. The CD curve of the compound was Boltzmann weighted follow UV correction.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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