Phytochemistry Letters 22 (2017) 9–12

Contents lists available at ScienceDirect

Phytochemistry Letters

journal homepage: www.elsevier.com/locate/phytol

Two pairs of new dihydrobenzophenanthridine alkaloid isolated from the root of *Macleaya cordata*

Kun Yu[a,b,1], Yi Peng[a,b,1], Zhixing Qing[b], Peng Yang[b], Zi Zuo[b], Pi Cheng[a], Xuefeng Mei[c,**], Jianguo Zeng[a,b,*]

[a] National and Local Union Engineering Research Center of Veterinary Herbal Medicine Resources and Initiative, Hunan Agricultural University, Changsha, 410128, China
[b] School of pharmacy, Hunan University of Chinese Medicine, Changsha 410208, China
[c] Pharmaceutical Analytical & Solid-State Chemistry Research Center, Shanghai Institute of Materia Medica, Chinese Academy of Science, Shanghai 201203, China

ARTICLE INFO

Keywords:
(±)(*S*)-6-((*R*)-1-hydroxyethyl) dihydrochelerythrine
(±)(*S*)-6-((*R*)-1-hydroxyethyl)-dihydrosanguinarine
Alkaloid
X-ray
Macleaya cordata

ABSTRACT

Two pairs of dihydrobenzophenanthridine alkaloid, named (±)(*S*)-6-((*R*)-1-hydroxyethy) dihydrochelerythrine (**1a, 1b**) and (±)(*S*)-6-((*R*)-1-hydroxyethyl)dihydro-sangunarine (**2a, 2b**) were isolated from the root of *Macleaya cordata.* Their chemical structures were elucidated by analysis of the spectroscopic data including one-dimensional (1D) and two-dimensional (2D) NMR spectra, and were further confirmed by X-ray crystallographic analysis.

1. Introduction

Macleaya cordata (Willd) R.Br., belonging to Papaveraceous family, is widely distributed in south and northwest China. In ancient China, this plant medicine was used for apostasis, anabrosis and empyrosis (Hu et al., 1975). Contemporary pharmacological studies demonstrated that *M. Cordata* had significant anti-microbial activity (Newton et al., 2002), anti-inflammatory (Kosina et al., 2010), anti-tumor (Ahmad et al., 2000) and animal growth promotion (Qing et al., 2015). Alkaloids were regarded the mainly bioactive constituents. As reported previously, more than thirty alkaloids were identified from this plant (Zhang et al., 2005; Ye et al., 2009; Feng et al., 2012; Qing et al., 2014, 2016). A series of products have been developed from these bioactive alkaloids. Sangrovit®, an extract of *M. Cordata*, which was used in Europe and China as a natural feed additive. In addition to these well-known compounds, a series of alkaloids which may have potential biological activities are still unknown, and further investigation is necessary. In this paper, two pairs of new dihydrobenzophenanthridine alkaloid named (±)(*S*)-6-((*R*)-1-hydroxyethyl) dihydrochelerythrine (**1a, 1b**) and (±)(*S*)-6-((*R*)-1-hydroxyethyl) dihydrosanguinarine (**2a, 2b**) were isolated from this plant medicine, and their structures were identified by HRMS, NMR spectra and X-ray crystallographic analysis (Fig. 1).

2. Result and discussion

2.1. Structure elucidation of compound 1

Compound **1** was obtained as a yellow powder, the molecular formula was established as $C_{23}H_{24}NO_5$ by HRMS (*m/z* 394.1647 $[M + H]^+$, calculated for 394.1649). The ^{13}C and DEPT spectra of **1** showed 23 carbons (Fig. S1), including ten C (sp^2) (δc 152.2, 148.3, 147.6, 146.9, 140.4, 131.1, 126.7, 126.7, 125.2, 123.9), six CH (sp^2) (δc 123.9, 119.9, 119.1, 111.9, 104.6, 100.5), two C (sp^3) (δc 69.3, 64.0), one OCH_2O (δc 101.2), two MeO (δc 61.0, 55.9), one Me (δc 43.8), and one MeN (δc 20.2). The ^1H NMR spectrum revealed six aromatic H-atoms (δ_H 7.68, 7.55, 7.45, 6.95, each d, J = 8.4; 7.65 and 7.10, each s), two methoxyls (δ_H 3.95, 3.91, s, each 3H), one *N*-methyl (δ_H 2.69, s, 3H) and one methylenedioxy (δ_H 6.03, s). These evidences indicated that **1** was a typical 6-substituent-dihydrobenzophenanthridine alkaloid (Hu et al., 2006; Di et al., 2009). In addition, a methyl (δc 20.2, δ_H 1.03) group and two methines (δ_H 4.32, δc 64.0; δ_H 3.55, δc 69.2) moieties were detected compared to the ^1H NMR of dihydrochelerythrine. The differences suggested that the group [$CH(OH)CH_3$] was included in compound **1**. In the HMBC spectrum (Fig. 2), the methylenedioxy (δ_H 6.03) correlations with C-2 (δc 147.6) and C-3 (δc 148.3), suggested that the methylenedioxy connected with C-2 and C-3. The two

* Corresponding author at: Hunan Agricultural University, Furong District, Changsha, Hunan, 410128, PR China.
** Corresponding author.
E-mail addresses: xuefengmei@simm.ac.cn (X. Mei), zengjianguo@hunau.edu.cn (J. Zeng).
[1] These authors contribution equally to this work.

http://dx.doi.org/10.1016/j.phytol.2017.08.002
Received 15 April 2017; Received in revised form 15 August 2017; Accepted 18 August 2017
1874-3900/ © 2017 Published by Elsevier Ltd on behalf of Phytochemical Society of Europe.

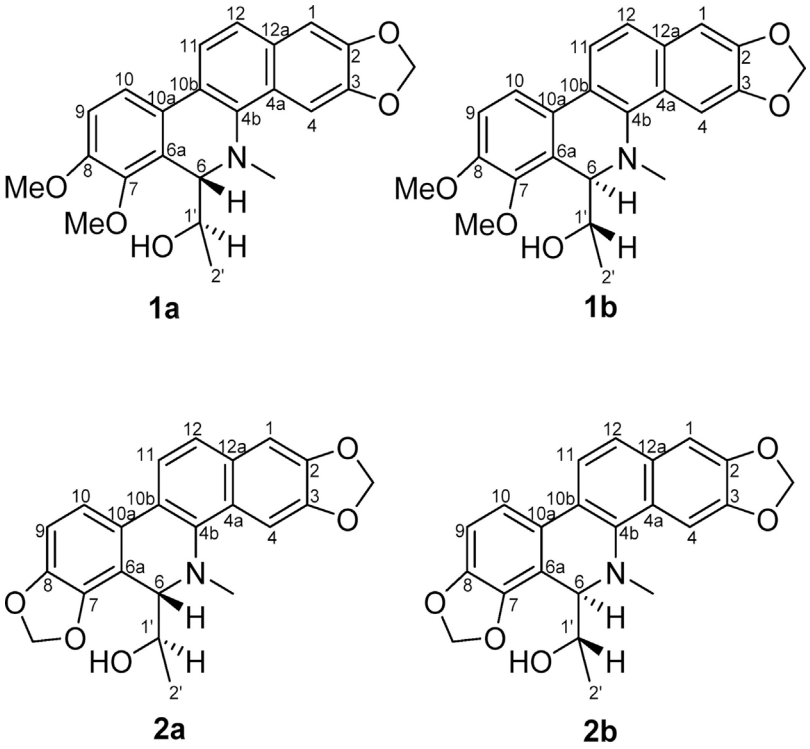

Fig 1. The chemical structures of alkaloids **1a**, **1b**, **2a** and **2b**.

methoxyls at δ_H 3.95 and 3.91 correlations with C-7 (δc 146.7) and C-8 (δc 152.1) respectively, which indicated that the two methoxyls connected with C-7 and C-8. The group $-CHOHCH_3$ (δ_H 3.58, 1.03) was assigned at C-6 (δc 64.0) due to the correlations of H-6 (δ_H 4.32) with C-1′ (δc 69.2) and H-2′ (δ_H 1.03) with C-6 (δc 64.0). Other significant HMBC correlations for the structural elucidation of compound **1** are given in Fig. 2. In addition, the chiral resolution of alkaloid **1** on a chiral column was performed, which demonstrated that compound **1** was a racemate (Fig. S3). X-ray diffraction experiments were further conducted in order to confirm the absolute configuration (Fig. 3). Finally, the structure of compound **1** was identified as (±)(*S*)-6-((*R*)-1-hydroxyethyl) dihydrochelerythrine (**1a, 1b**).

2.2. Structure elucidation of compound 2

Compound **2** was obtained as a yellow powder, the molecular formula was established as $C_{22}H_{20}NO_5$ by HRMS *m/z* 378.1338 $[M + H]^+$ (calculated for 378.1341). The ^{13}C NMR and DEPT spectra of **2** showed 22 carbons (Fig. S2), including ten C (sp^2) (δc 148.7, 147.6, 147.1, 146.2, 140.2, 131.1, 126.9, 126.1, 123.9, 114.7), six CH (sp^2) (δc 123.9, 120.2, 116.7, 107.9, 104.9, 100.6), two C (sp^3) (δc 69.2, 64.3), two OCH_2O (δc 101.5, 101.2), one Me (δc 20.1), and one MeN (δc 44.0). The ^1H NMR spectrum revealed six aromatic H-atoms (δ_H 7.68, 7.46, 7.36, 6.89, each d, J = 8.4; 7.66 and 7.09, each s), one *N*-methyl (δ_H 2.67), two methylenedioxys (δ_H 6.01, 6.05). These data indicated that compound **2** was also a dihydrobenzophenanthridine alkaloid (Hu et al., 2006). the mere differences between **2** and **1** was the two methoxyls at C-7 and C-8 was replaced by a methylenedioxy, which was further confirmed by the HMBC correlations of methylenedioxy (δ_H 6.05) with C-7 (δc 146.2) and C-8 (δc 147.1) (Fig. 2). In additional, compound **2** was also regarded as a pair of racemate by the X-ray and chiral HPLC separation experiments (Fig. 3 and S4). Finally, compound **2** was identified as (±)-(*S*)-6-((*R*)-1-hydroxyl) dihydrosanguinarine (**2a, 2b**).

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on bruker axs, IR spectra were taken on Nicolet infrared spectrometer with KBr disc technique. 1D and 2D NMR spectra were recorded on a Bruker ACF-400 (the ^{1}HNMR spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz). The mass was collected by an Agilent 1290 HPLC system coupled with a 6350 Q-TOF/MS accurate-mass spectrometer. The chiral HPLC separation experiment was performed on an Agilent 1260 HPLC system coupled with a CHIRALCEL OJ-H (Lot No. OJH0CE-UC023) chiral column. Column chromatography was performed on silica gel (200–300 or 300–400 mesh; QingDao Marine Chemical Factory, QingDao, RP China). The X-ray data were collected by on a Bruker APEX-II CCD

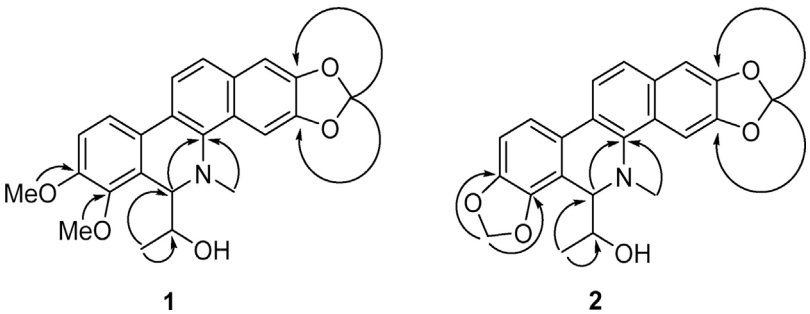

Fig. 2. Key HMBC correlation of alkaloids **1** and **2**.

Download English Version:

https://daneshyari.com/en/article/5175791

Download Persian Version:

https://daneshyari.com/article/5175791

Daneshyari.com