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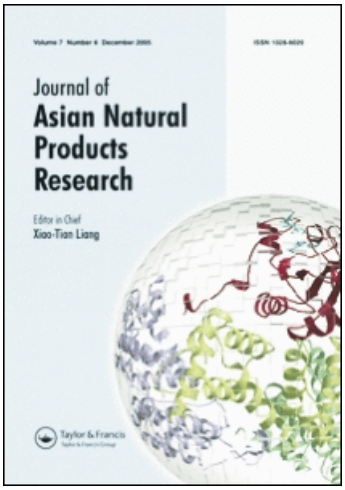

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A NEW SESQUITERPENE LACTONE GLUCOSIDE FROM *IXERIS SONCHIFOLIA*

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A new sesquiterpene lactone glucoside, Ixerin Z_1 (**1**), was isolated from the whole plants of *Ixeris sonchifolia* (Bge.) Hance, along with 15 known compounds. The structure of **1** was elucidated as 1(10),3,11(13)-guaiatriene-12,6-olide-2-one-3-O-[6'-(*p*-hydroxyphenylacetyl)]-glucopyranoside by spectroscopic methods including 2D-NMR techniques.

Keywords: *Ixeris sonchifolia*; Compositae; Ixerin Z_1

INTRODUCTION

Ixeris sonchifolia (Bge.) Hance (Family Compositae) is abundantly distributed throughout the northeastern China. It is a small perennial herb, about 0.4 m tall commonly found in dry places. It has been used as a folk medicine in invigorating circulation of blood, normalizing menstruation and eliminating blood stasis to relieve pain [1]. Previous phytochemical studies on other species of this genus revealed the presence of sesquiterpene lactones [2–7]. In our investigations of biologically active and/or structurally novel substances from *I. sonchifolia*, we examined the constituents of the plant. This paper describes the isolation and structure determination of a new sesquiterpene lactone glucoside, Ixerin Z_1 (**1**).

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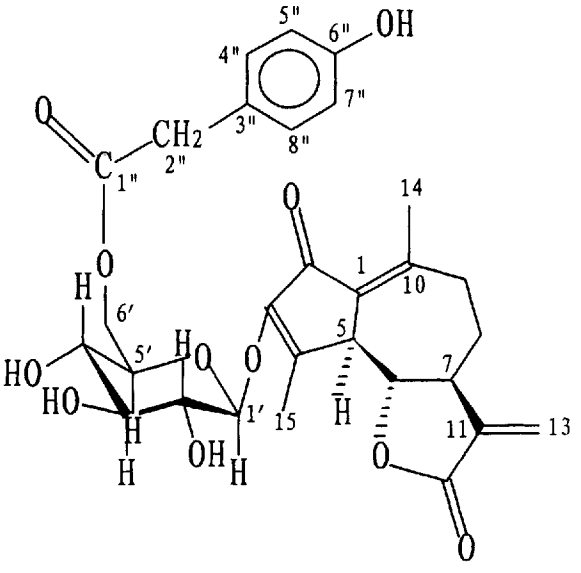

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RESULTS AND DISCUSSION

The methanol soluble fraction yielded Ixerin Z_1 (**1**), which was crystallized as white needles. A molecular formula of $C_{29}H_{32}O_{11}$ for compound **1** was assigned from its ESI-MS ($M^+ + Na = 579$) and EI-MS [$M^+ + 1 - (C_6H_{11}O_5 + C_8H_6O_2) = 260$]. The IR spectrum of **1** showed the presence of hydroxy groups (3400 cm^{-1}), broad carbonyl bands at 1769 and 1670 cm^{-1} indicating the presence of at least two different types of carbonyl groups, double bond (1640 cm^{-1}) and aromatic ring (1616, 1517 cm^{-1}). On acid hydrolysis, compound **1** gave glucose by comparison with authentic samples on co-TLC and paper chromatography. The ^{1}H-NMR spectrum (Tab. I) contained the characteristic signals located at δ 6.14 (1H, *d*, $J = 3.0$ Hz, H-13a) and δ 5.33 (1H, *d*, $J = 3.0$ Hz, H-13b) of an α-methylene-γ-lactone moiety. Signals for two vinyl methyls at δ 2.32 (3H, brs, H-15) and δ 2.47 (3H, brs, H-14) and a sugar moiety were also observed. A double doublet at δ 3.26 (1H, $J = 10.2$ Hz, 12.2 Hz) was assigned to H-6, which was coupled with H-5 at δ 3.30 (1H, *d*, $J = 10.2$ Hz) and H-7 at δ 2.75 (1H, brt, $J =$ 12.2 Hz). This indicated the *trans*-diaxial relationship of the vicinal protons. The stereochemistry of these protons was considered to be H-5 α, H-6 β, since H-7 in naturally occurring guaianolides has α-orientation [8].

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TABLE I ^{1}H-NMR spectral data of **1** in pyridine-d_5

H	**1**	*H*	**1**
H-5	3.30 *d* (J = 10.2 Hz)	H-2′	4.23 *dd* (J = 7.5, 8.0 Hz)
H-6	3.26 *t* (J = 10.2, 12.2 Hz)	H-3′	4.29 *dd* (J = 8.0, 8.0 Hz)
H-7	2.75 brt (J = 12.2 Hz)	H-4′	4.13 *dd* (J = 8.0, 8.0 Hz)
H-8a	1.87 brd (J = 11.1 Hz)	H-5′	4.10 m
H-8b	1.08 *dd* (J = 12.2, 11.1 Hz)	H-6′a	4.99 brd (J = 11.4 Hz)
H-9a	2.28 overlapped	H-6′b	4.73 *dd* (J = 11.4, 6.0 Hz)
H-9b	2.08 m	H-2″	3.69 s
H-13	6.14 *d* (J = 3.0 Hz)	H-4″	7.30 *d* (J = 8.4 Hz)
	5.33 *d* (J = 3.0 Hz)	H-5″	7.10 *d* (J = 8.4 Hz)
H-14	2.47 brs	H-7″	7.10 *d* (J = 8.4 Hz)
H-15	2.32 brs	H-8″	7.30 *d* (J = 8.4 Hz)
H-1′	6.12 *d* (J = 7.5 Hz)		

TABLE II ^{13}C-NMR spectral data of **1** in pyridine-d_5

Carbon	^{13}*C-NMR*	*DEPT*	*HMBC*	*Carbon*	^{13}*C-NMR*	*DEPT*	*HMBC*
1	152.6	C	5,9,14	1′	101.4	CH	2′,5′
2	188.5	C		2′	74.8	CH	1′,3′,4′
3	153.2	C	1′,5,15	3′	77.6	CH	4′,5′
4	146.6	C	5,15	4′	70.7	CH	3′,5′,6′
5	47.5	CH	6,15	5′	75.1	CH	1′,3′,4′,6′
6	84.6	CH	5,7,8	6′	64.1	CH_2	4′,5′
7	51.9	CH	6,8,13	1″	171.6	C	6′,2″
8	23.6	CH_2	6,7,9	2″	39.7	CH_2	4″,8″
9	36.4	CH_2	8,14	3″	124.6	C	2″,5″,7″
10	129.1	C	5,9,14	4″	130.5	CH	2″,5″,7″
11	139.1	C	13	5″	115.8	CH	4″,8″
12	168.6	C	13	6″	157.3	C	4″,5″,7″,8″
13	117.5	CH_2		7″	115.8	CH	4″,8″
14	21.2	CH_3	9	8″	130.5	CH	2″,5″,7″
15	14.4	CH_3	5				

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The signals located at δ 7.30 (2H, *d*, J = 8.4 Hz) and 7.10 (2H, *d*, J = 8.4 Hz) showed the presence of a 1,4-disubstituted aromatic ring. The ^{13}C-NMR data (Tab. II) of **1** showed the presence of 29 carbons. Of the fifteen unsaturated carbons, three were attributed to a lactone carbonyl at δ 168.6 (C-12), an α, β-unsaturated ketone carbonyl at δ 188.5 (C-2) and an ester carbonyl at 171.6 (C-1″), six were olefinic carbons and six were aromatic carbons; of the 14 alkyl carbons, seven were oxygen-bearing carbons of which six were derived from the glucose moiety. The remaining signals were those of two methines, three methylenes and two methyls. In the HMBC spectrum of compound **1**, the cross peaks between C-1″ with H-6′a and H-6′b confirmed that *p*-hydroxyphenylacetic acid was esterified at C-6 of the glucose moiety (Tab. II). The HMBC spectrum also displayed cross peaks between C-3 with H-1′, showing that the glucose moiety was affixed to C-3

of the aglycone. The absolute configuration of the glucose moiety could not be deduced from the NMR data. The anomeric configuration was determined to be β from the $J_{H1'-H2'}$ value ($J = 7.5$ Hz) [9]. Based on the above evidence, **1** was identified as 1(10),3,11(13)-guaiatriene-12,6-olide-2-one-3-O-[6′-(*p*-hydroxyphenylacetyl)]-glucopyranoside.

EXPERIMENTAL SECTION

General Experimental Procedures

Instrumentation: ^{1}H-NMR (300 MHz, pyridine-d_5) and ^{13}C-NMR (75 MHz, pyridine-d_5), and 2D-NMR spectra were recorded on a Bruker AM 300 FT-NMR spectrometer using tetramethylsilane (TMS) as internal standard. Electrospray Ionization Mass (ESI-MS) and EI-MS were recorded on Finnigan LCQ LC/ESI-MS and VG 7070E spectrosmeter. IR spectrum was taken on a Bruker IFS 55 spectrometer and recorded in KBr pellets. Column chromatography was performed on silica gel (200 ~ 300 mesh, Qingdao, China), and the TLC analyses were carried out using glass precoated silica gel plates.

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Plant Material

The plant material was gathered in Liaoning Province, China, in June, 1996, and a voucher specimen (No.10082), identified by Prof. Qi-Shi Sun, is deposited in the Herbarium of the Department of Chinese Traditional Medicines, Shenyang Pharmaceutical University.

Extraction and Isolation

The material was shade-dried and after grinding, 7.5 Kg were extracted with hot 70% EtOH three times. After removal of the solvent by evaporation, the EtOH extract (1500 g) was extracted three times each with petroleum ether (60 ~ 90°C), $CHCl_3$, and MeOH, under reflux. The MeOH extract was concentrated to a syrup (150 g), and then subjected to chromatographic separation on a silica gel column (200 ~ 300 mesh, 1400 g). The compounds of the mixture were eluted with $CHCl_3$ (4 L) and with $CHCl_3$: MeOH (50 : 1, 30 : 1, 20 : 1, 12 : 1, 10 : 1, 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, each 10 L), subsequently 10 fractions were obtained. Rechromatography (60H silica gel, Qingdao, China) of the three fractions (6 g) [$CHCl_3$: EtOAc (7 : 3, v/v) as eluent] gave compound **1** (20 mg).

Ixerin $\mathbf{Z}_1$ $C_{29}H_{32}O_{11}$. Fine white needles. IR ν_{max}^{KBr} cm^{-1}: 3440, 1770, 1670, 1652, 1620, 1517, 1446, 1385, 1253, 1070; positive ion ESI-MS m/z: 579 $[M+Na]^+$, 557 $[M+1]^+$, 260 $[M+1\text{-}(C_6H_{11}O_5+C_8H_6O_2)]^+$; EI-MS (probe) 70ev, m/z (rel.int): 260 $[M+1\text{-}(C_6H_{11}O_5+C_8H_6O_2)]^+$ (7), 242 (2), 189 (3), 152 (17), 134 (12), 107 (100); ^1H and ^{13}C-NMR data are listed in Tables I and II.

Acid hydrolysis of **1** Compound **1** was refluxed in 2.0 mol/L HCl at 100°C for 2 h. After cooling to room temperature, the reaction mixture was neutralized with Ag_2CO_3 and centrifuged, and then the supernatant was evaporated on a water bath and subjected to TLC analysis on GF_{254} [using $CHCl_3-MeOH-H_2O$ (6:4:1)] and paper chromatography [using *n*-BuOH – HOAc – H_2O (4:1:5)] by comparison with authentic samples.

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