

*Full Length Research Paper*

# A new alkaloid-aluminum glycoside isolated from *Rhizoma Sparganii* (*Sparganium stoloniferum* Buch. - Ham.)

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**Rhizoma Sparganii is a traditional Chinese medicine for bad stomach. A new N-heterocyclic Al complex glycoside was isolated from aqueous extractive of dried rhizome of *Sparganium stoloniferum* by column chromatography, and its structure was assigned by spectroscopic methods. The new alkaloid glycoside was named Grailsine-Al-glycoside, yield 5.99% (dry weight / dry rhizome weight). Grailsine-Al-glycoside is the first alkaloid that has been isolated from *Rhizoma Sparganii* materia medica and, its structure indicates an abundant aluminum complex compound existence in higher plant.**

**Key words:** *Rhizoma Sparganii*, Grailsine-Al-glycoside, alkaloid, aluminum; al-rich plant.

## INTRODUCTION

*Rhizoma Sparganii*, dried rhizome of *Sparganium stoloniferum* Buch. -Ham., is a traditional Chinese folk medicine frequently used in the treatment of functional dyspepsia disease (Chinese Pharmacopoeia Commission, 2010). Though researchers have isolated a few flavonoids and phenylpropanoid glycosides from ethyl acetate extracts of *rhizoma sparganii* (Shirota et al., 1996, 1997; Zhang et al., 1996), the phytochemical components of *Rhizoma Sparganii* potentially responsible for the stomach trouble treatment are still unclear.

## MATERIALS AND METHODS

### Herb materials

*Rhizoma Sparganii* pieces were purchased from Yi-Kang Chain the State Food and Drug Administration of China. A voucher specimen was deposited in Key Laboratory of Resource Biology and Biotechnology in Western China.

Medicine Co. (Xi'an, China). The materia medica standardization was consistent with the good supplying practice (GSP) provided by the *Rhizoma Sparganii* powder was immersed in boiling distilled

water 4 h and then the solution was concentrated at 80°C under 0.7 Pa pressure as crude extract sample, the yield was 9.81% (dry weight/dry rhizome weight). The extract was deposited by methanol to remove impurities and the supernatant was concentrated again for column chromatography.

### Methods

Normal-phase column was packed with Pharmacia Sephadex G-25(Fine). <sup>1</sup>H and <sup>13</sup>C spectra were recorded on Varian INOVA-400MHz spectrometers. TOF-MS spectra were obtained on AXIMA-CFR™ plus MALDI-TOF Mass Spectroscopy. Elements were analyzed on VarioEL III, and monosaccharide composition was analyzed by general method (Endwin et al., 1967).

## RESULTS

The new alkaloid-glycosides was isolated from aqueous extract of *Rhizoma Sparganii* pieces by column chromatography method, yield 5.99% (dry weight/dry rhizome weight), and it was named Grailsine-Al-glycoside (Figure 1). White powder or brown gelatin, C<sub>23</sub>H<sub>41</sub>O<sub>14</sub>N<sub>3</sub>Al (610.57), MALDI-TOFMS *m/z* 611.23 [M]<sup>+</sup>, 613.81 [M+2H]<sup>+</sup>, 615.81 [M+4H]<sup>+</sup>. <sup>1</sup>H NMR, <sup>13</sup>C NMR data see Table (Table 1).

Because <sup>1</sup>H NMR data is helplessness on hetero polysaccharide structure analysis, monosaccharide composition was further tested to help analysis the

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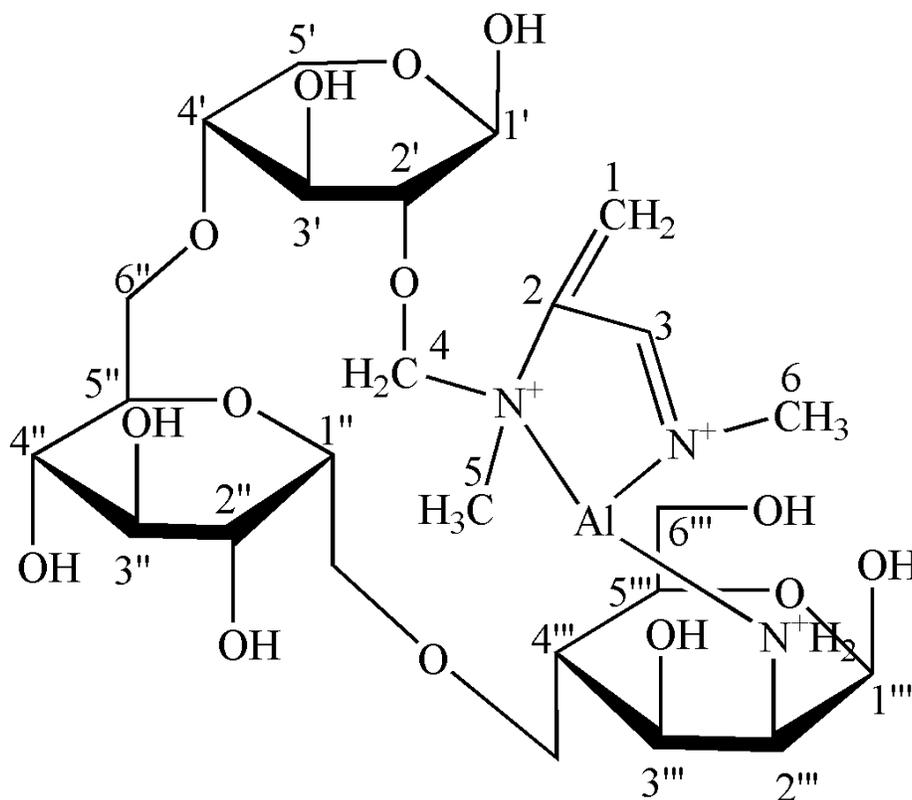


Figure 1. Structure of Grailsine-Al-glycoside.

trisaccharide structure. 2 mol/L final concentration trifluoroacetic acid 100 °C, 4 h decomposition, acetylation and further gas chromatography results dedicated that, the trisaccharide linked to Grailsine-Al complex was composed by same amount of Glucose, Xylose and Mannose. Refer to the reported oligosaccharides  $^{13}\text{C}$  NMR data,  $^{13}\text{C}$  NMR results in this investigation confirmed the glycoside is  $\beta$ -Xylose (4 $\rightarrow$ 6)- $\alpha$ -Glucose (1 $\rightarrow$ 4)- $\beta$ -Mannose osamine (Figure 1).

In addition, the Grailsine-Al-glycoside solution has a slow self oxidation reaction when it was exposed to the air, the oxidation products are Grailsine-glycoside,  $\text{C}_{23}\text{H}_{38}\text{O}_{15}\text{N}_2$  (582.55), MALDI-TOFMS  $m/z$  582.33  $[\text{M}]^+$  and, a great quantity of white power. The white power mp 2050 °C, soluble in both NaOH and HCl solution, was verified as alumina. These results showed that there is an aluminium complexation on Grailsine-glycosides.

## DISCUSSION

In this investigation a new Al complex alkaloid-glycoside, named Grailsine-Al-glycoside was isolated from the traditional Chinese medical plant *S. stoloniferum*. Grailsine-Al-glycoside is the first alkaloid that has been isolated from *Rhizoma Sparganii*, mean while it account

for 61.4% dry weight of the *Rhizoma Sparganii* aqueous extract. People generally consider plant or animal organisms should not accumulate aluminum. Moreover, researches have confirmed that Al accumulate can induce neurotoxicity in people and a higher environment Al level can severely inhibit plant root elongation (Crapper-McLachlan, 1986; Eichhorn, 1993; Ma et al., 2001; Matsumoto, 2000; Polizzi et al., 2002; Poschenrieder et al., 2008). However, the discovery of Grailsine-Al-glycoside structure indicated that there is an abundant organic-Al complex existence in higher plants *S. stoloniferum*.

Aluminum can combine with gastric acid then form a colloid protective film on the ulcer surface of stomach. Therefore, aluminium is the major components of drugs currently used on treatment of hyperacidity and ulcer. It has been confirmed that, most higher plants contain only trace aluminum element, the average  $[\text{Al}]^{3+}$  level of common higher plants is no more than 10 mg/kg (Lopez et al., 2000). A few Al rich plant such as teas, are famous for its 90 ~ 500 mg/kg  $[\text{Al}]^{3+}$  content (Fung et al., 2009; Morita et al., 2008; Shu et al., 2003; Wong et al., 2003). However, in a further study of this investigation,  $[\text{Al}]^{3+}$  content of *Rhizoma Sparganii* from three different province of China (12 batch) is 8.25 ~ 12.38 g/kg. That is a thousand times higher than normal higher plant.

**Table 1.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data of Grailsine-Al-glycoside.

Parameters	$\delta_{\text{C}}$ ppm	$\delta_{\text{H}}$ ppm
<b>Grailsine</b>		
C1	134.439	
C2	42.882	4.032 (2H, s)
C3	159.205	2.803 (1H, s)
C4	26.257	3.561 (2H, s)
C5	22.350	3.316 (3H, s)
C6	29.950	1.657 (3H, s)
<b><math>\beta</math>-Xylose</b>		
C1'	98.312	
C2'	83.354	
C3'	76.532	
C4'	78.354	
C5'	65.763	
<b><math>\alpha</math>-Glucose</b>		
C1''	100.488	
C2''	71.997	
C3''	73.877	
C4''	69.930	
C5''	71.601	
C6''	66.264	
<b><math>\beta</math>-Mannose osamine</b>		
C1'''	94.491	
C2'''	56.702	
C3'''	64.780	
C4'''	78.158	
C5'''	75.157	
C6'''	63.140	

Measurements were performed in  $\text{D}_2\text{O}$ .  $^1\text{H}$  NMR 400 MHz,  $^{13}\text{C}$  NMR 100 MHz.

In conclusion, *S. stoloniferum* is the plant that contains the highest  $[\text{Al}]^{3+}$  level that have ever been known. Intake of 9 g conventional *Rhizoma Sparganii* dose equivalent intake half amount Al that commercial stomach medicine contains. Besides the already reported compounds, aluminum element is no doubt an active component of *Rhizoma Sparganii* on stomach disease treatment.

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