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Two new steroidal saponins from the rhizomes of Dioscorea zingiberensis

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[ABSTRACT]

AIM: To investigate the chemical constituents of Dioscorea zingiberensis C. H. Wright.

METHODS: The compounds were isolated by various chromatographic techniques, and the structures of the new steroidal saponins were elucidated by extensive 1D- and 2D-NMR, MS, and IR spectral analysis.

RESULTS: The 70% EtOH extract of the rhizomes of Dioscorea zingiberensis afforded two new steroidal saponins, zingiberenosides A (1) and B (2), along with eight known analogues, 3β , 26-dihydroxy-25(R)-furosta- \triangle ^{5, 20(22)}-diene-3-O- α -L- rhamnopyranosyl- $(1 \rightarrow 2)$ -O- β -D-glucopyranoside (3), methyl parvifloside (4), deltoside (5), methyl deltoside (6), zingiberensis new saponin (7), deltonin (8), progenin III (9) and diosgenin-diglucoside (10).

CONCLUSION: Two new steroidal saponins were isolated from Dioscorea zingiberensis and their structures determined.

[KEY WORDS] Dioscorea zingiberensis; Dioscoreaceae; Steroidal saponins; Zingiberenoside

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Introduction

Dioscorea zingiberensis C. H. Wright, common name 'Huang Jiang', is a perennial herb, and is distributed widely in Henan, Hubei, Sichuan, and the south of Shanxi provinces [1-2]. It is used to treat cough with lung heat, pyretic stranguria, anthracia, swelling, ulcers, and sprains. As an important species of the Dioscoreaceae, D. zingiberensis has attracted much attention for the high content of diosgenin and steroid saponins [3], as well as excellent pharmacologic action, such as reducing the content of cholesterol

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in blood [4], and decreasing stenocardia and regulating metabolism [5]. Furthermore, its total steroidal saponins could treat atherosclerosis, high blood fat, wheeze, inflammation. and tumors [6-7]. Previous phytochemical investigations of its rhizomes led to the isolation of several steroidal saponins [5, 8-15]. In this paper, the isolation and structural elucidation of two new steroidal saponins and eight known derivatives from the 70% EtOH extract of the dried rhizome of D. zingiberensis are reported.

Results and Discussion

A 70% EtOH extract of the commercially available rhizomes of D. zingiberensis was fractionated by macroporous resin and silica gel, and then separated by ODS column chromatography and semi-preparative HPLC to afford two new steroidal saponins, zingiberenoside A (1) and zingiberenoside B (2), together with eight known analogues (Fig. 1). The structures of the new compounds were elucidated by extensive 1D- and 2D-NMR, MS, and IR spectral analyses.

Compound 1 was obtained as a white amorphous powder, and was deduced to possess a furostanol group based on TLC using Ehrlich's reagent [20]. The IR spectrum showed absorp-



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Fig. 1 Structures of compounds 1-10

tion bands of hydroxyl (3 421 cm $^{-1}$), methyl (2 930 cm $^{-1}$), and olefinic (1 644 cm $^{-1}$) groups. The molecular formula was assigned to be $C_{51}H_{82}O_2$ on the basis of positive HRESI-MS

 $[M + Na]^+$ ion peak at m/z 1069.520 32 (Calcd. 1069.519 54). The 1 H and 13 C NMR (pyridine- d_5 , 500/125 MHz) data (Tables 1 and 2), assigned by 1 H- 1 H COSY, HSQC, and

Table 1 13 C NMR data for the aglycone of compounds 1–10 (in pyridine- d_5 , 125 MHz)

No.	1	2	3	4	5	6	7	8	9	10
1	37.9	37.9	37.9	37.8	37.9	37.8	37.8	37.8	37.8	37.8
2	30.5	30.5	30.6	30.5	30.5	30.5	30.5	30.5	30.5	30.9
3	78.4	78.4	78.7	78.5	78.6	78.6	78.7	78.5	78.6	78.7
4	39.3	39.3	39.4	39.3	39.3	39.3	39.3	39.3	39.3	39.6
5	141.2	141.2	141.2	141.2	141.2	141.2	141.2	141.1	141.2	141.2
6	122.2	122.2	122.2	122.2	122.2	122.1	122.1	122.1	122.1	122.1
7	32.8	32.8	32.8	32.5	32.0	32.0	32.7	32.6	32.7	32.7
8	31.8	31.8	31.8	32.0	31.2	31.2	32.0	32.0	32.0	32.0
9	50.7	50.7	50.7	50.7	50.7	50.7	50.6	50.6	50.6	50.6
10	37.5	37.5	37.5	37.4	37.6	37.5	37.5	37.5	37.4	37.5
11	21.6	21.6	21.6	21.4	21.4	21.4	21.5	21.4	21.5	21.5
12	40.0	40.0	40.0	40.1	40.1	40.3	40.2	40.2	40.2	40.2
13	43.8	43.8	43.8	41.2	41.1	41.1	40.8	40.8	40.8	40.8
14	55.3	55.3	55.3	56.9	56.9	56.9	57.0	57.0	57.0	57.0
15	34.9	34.8	34.9	32.7	32.6	32.8	32.6	32.7	32.6	32.6
16	84.8	84.8	84.8	81.6	81.6	81.4	81.5	81.5	81.5	81.5
17	64.9	64.9	64.9	64.6	64.2	64.5	63.3	63.2	63.2	63.2
18	14.5	14.5	14.5	16.6	16.6	16.6	16.7	16.7	16.7	16.7
19	19.8	19.8	19.8	19.7	19.7	19.7	19.7	19.7	19.7	19.8
20	103.9	103.9	103.9	40.9	40.8	40.0	42.3	42.3	42.4	42.3
21	12.2	12.2	12.1	16.6	16.8	16.6	15.4	15.4	15.4	15.4
22	152.8	152.7	152.8	113.0	111.0	113.0	109.6	109.6	109.6	109.6
23	33.9	33.9	33.8	37.4	37.5	37.6	32.2	32.2	32.2	32.2
24	24.1	24.1	24.1	28.5	28.7	28.5	29.6	29.6	29.6	29.6
25	31.8	31.8	31.8	34.6	34.6	34.6	30.9	31.0	30.9	30.9
26	75.3	75.3	75.3	75.6	75.6	75.6	67.2	67.2	67.2	67.2
27	17.7	17.7	17.7	17.5	17.8	17.5	17.7	17.7	17.7	17.7
-OCH ₃				47.6		47.6				

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