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Steroidal saponins from fresh stem of *Dracaena cochinchinensis*

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Abstract

A further phytochemical investigation on the fresh stem of *Dracaena cochinchinensis* yielded 18 steroidal saponins. Fourteen of which are new compounds, designated as 25(*R*,*S*)-dracaenosides E–H, M, O–Q, dracaenosides I–L, *R*, and 25(*S*)-dracaenoside N. Their structures were determined by detailed spectroscopic analysis, including extensive 1D and 2D NMR data, and the result of hydrolytic reaction.

Keywords: *Dracaena cochinchinensis*; Agavaceae; Steroidal saponins; Dracaenosides E–R

1. Introduction

The genus *Dracaena* (Agavaceae) containing about 60 species is distributed from the Old World tropic region to Canary Island. The resins from stems of several species of this genus as a source of dragon's blood were used as traditional medicine from ancient time. In China, the red resin of *Dracaena cochinchinensis* (Lour.) S.C. Chen, called "longxuejie", was used as Chinese dragon's blood for promoting blood circulation and the treatment of traumatic and visceral hemorrhages [1]. In previous study, a lot of phenolic compounds were isolated from the resins [2–6], and steroids, such as protogracillin, gracillin, protodioscin and dioscin, were obtained from the fruits of this plant [7]. Recently, we reported four new pregnane glycosides, dracaenosides A–D (**1**–**4**) from the fresh stem of *D. cochinchinensis* [8,9]. In a continuation of a study on Chinese dragon's blood and its origin plants, we have further phytochemical investigated the fresh stem, resulting in the isolation of 14 new steroidal saponins, designated as 25(*R*,*S*)-dracaenosides E–H (**5**–**8**), M (**13**), and O–Q (**15**–**17**), dracaenosides I–L (**9**–**12**) and *R* (**18**), and 25(*S*)-dracaenoside N (**14**), together with four known 25(*R*,*S*)-steroid saponins epimers (**19**–**22**). The present paper deals with the experimental details of separation and structure elucidation of these new compounds on the basis of the spectroscopic analysis, including 2D NMR techniques, and the result of hydrolytic reaction.

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2. Experimental

2.1. General methods

Optical rotations were measured on a SEPA-3000 automatic digital polarimeter. NMR spectra were run on Bruker AM-400 (for ^{1}H NMR and ^{13}C NMR) and DRX-500 (for 2D NMR) instruments with TMS as internal standard; IR spectra were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. FAB-MS spectra were recorded on a VG Auto Spec-300 spectrometer. UV spectra were obtained on a Shimadzu double-beam 210A spectrophotometer. GC–MS was run on Fisons MD-800 GC/MS instruments using 30QC2/AC-5 fused silica capillary column (30 m × 0.25 mm) in following conditions—filament current: 4.2 A; column temperature: 180/260 °C, programmed increase, 5 °C/min; carrier gas: He; head pressure: 12 psi; EI-MS: 70 eV; ion source temperature: 250 °C. Silica gel (200–300 mesh and 10–40 μm), RP-18 (40–63 μm) and Sephadex LH-20 were used for column chromatography.

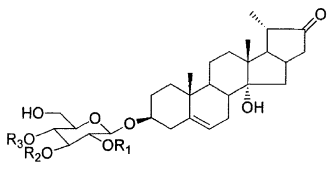
2.2. Plant material

The fresh stems of *D. cochinchinensis* were collected from Xishuangbanna, Yunnan, China, and a voucher specimen is deposited at the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

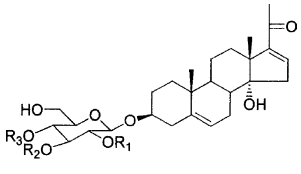
2.3. Extraction and isolation

The chipped fresh stem of *D. cochinchinensis* (25.0 kg) was extracted with hot MeOH. The MeOH extract was

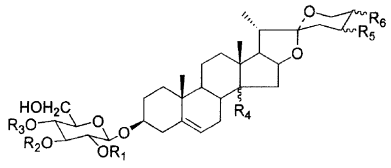
condensed under reduced pressure. The viscous concentrate was partitioned between H_2O and *n*-BuOH successively. The *n*-butanol fraction was submitted through a column chromatography of high porous absorption resin (Diaion HP-20), eluting with H_2O and methanol. The methanol fraction (150 g) was repeatedly column chromatographed (CC) over normal and reverse phase silica gel to afford three fractions (Frs. I–III). Fr. I was subjected to ODS CC eluting with MeOH–H_2O and silica gel with $CHCl_3$–MeOH–H_2O to give compounds **1** (40 mg), **2** (26 mg), **3** (36 mg), **4** (25 mg), **5** (30 mg) and **6** (17 mg). Fr. II was subjected to ODS CC eluting with MeOH–H_2O and silica gel CC with $CHCl_3$–MeOH–H_2O to give **19** (50 mg), **20** (56 mg), **21** (200 mg), **22** (67 mg), **7** (33 mg), **8** (150 mg), **9** (677 mg), **10** (56 mg), **11** (100 mg), **12** (200 mg), **13** (123 mg), **14** (70 mg), **15** (15 g) and **16** (2.5 mg). Fr. III was subjected to ODS CC eluting with MeOH–H_2O and silica gel CC with $CHCl_3$–MeOH–H_2O to give **15** (4.0 g), **16** (1.5 g), **17** (35 mg) and **18** (18 mg).



	R_1	R_2	R_3
1	rhap	H	rhap
2	rhap	glcp	H



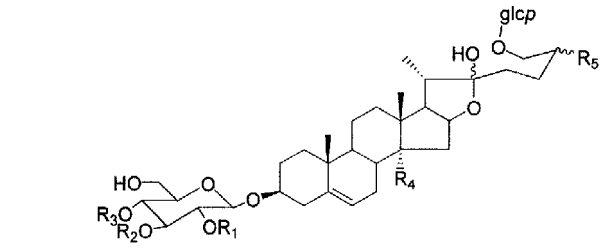
	R_1	R_2	R_3
3	rhap	H	rhap
4	rhap	glcp	H



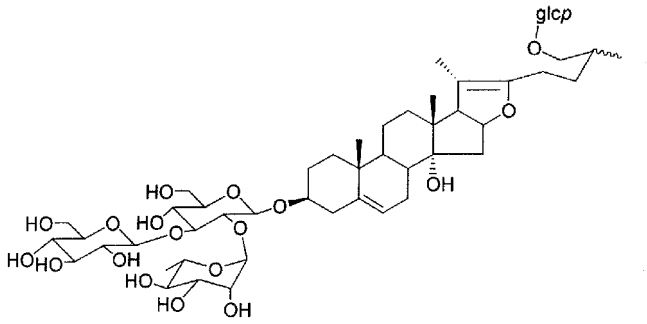
	R_1	R_2	R_3	R_4	R_5	R_6
5	H	H	rhap	OH	H	eq+ax Me
6	rhap	H	H	OH	H	eq+ax Me
7	rhap	H	rhap	OH	H	eq+ax Me
8	rhap	glcp	H	OH	H	eq+ax Me
9	rhap	glcp	H	H	H	$=CH_2$
10	H	glcp	rhap	OH	H	eq CH_2OH
11	rhap	H	rhap	OH	OH	ax Me
12	rhap	glcp	H	OH	OH	ax Me
19	rhap	H	rhap	H	H	eq+ax Me
20	rhap	glcp	H	H	H	eq+ax Me

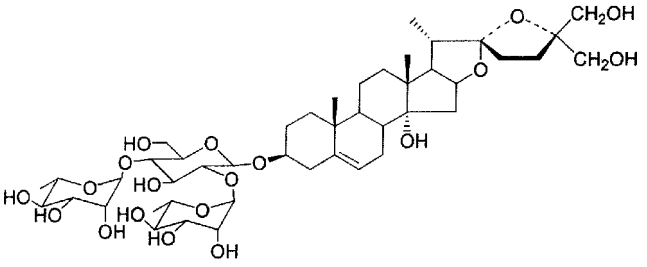
2.3.1. 25(R,S)-Dracaenoside E (5)

White amorphous powder, $C_{39}H_{62}O_{13}$, $[\alpha]_D^{28}$ − 71.55° (MeOH, $c = 0.2$). Negative ion HRFAB-MS, *m/z*: 737.4066 $[M - H]^-$ (calcd. 737.4112). Negative ion FAB-MS, *m/z*: 738 $[M]^+$, 592 $[M - 146]^+$, 429 $[M - 146 - 162 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3428 (br, OH), 2940 (CH), 2868 (CH), 1645, 917, 898, 878; ^1H NMR (pyridine-d_5), δ (ppm): 5.89 (1H, brs, 1″-H), 5.40 (1H, brs, 6-H), 4.94 (1H, d, J = 7.70 Hz, 1′-H), 1.72 (3H, d, J = 5.85 Hz, 6″-CH_3), 1.18 (3H, d, J = 6.25 Hz, 21-CH_3, 25*R*), 1.19 (3H, d, J = 6.0 Hz, 21-CH_3, 25*S*), 1.07 (3H, s, 18-CH_3), 0.99 (3H, s, 19-CH_3), 1.07 (3H, d, J = 2.10 Hz, 27-CH_3, 25*S*), 0.67 (3H, d, J = 5.50 Hz, 27-CH_3, 25*R*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.



	R_1	R_2	R_3	R_4	R_5
13	H	H	rhap	OH	eq+ax Me
14	rhap	H	H	OH	eq+ax Me
15	rhap	H	rhap	OH	eq+ax Me
16	rhap	glcp	H	OH	eq+ax Me
21	rhap	H	rhap	H	eq+ax Me
22	rhap	glcp	H	H	eq+ax Me





2.3.2. 25(R,S)-Dracaenoside F (6)

White amorphous powder, $C_{39}H_{62}O_{13}$, $[\alpha]_D^{28}$ − 45.17° (MeOH, $c = 0.2$). Negative ion HRFAB-MS, *m/z*: 737.4126 $[M-H]^-$ (calcd. 737.4112). Negative ion FAB-MS, *m/z*: 737 $[M-H]^-$, 592 $[M-146]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3420 (br, OH), 2938, 2866, 1642, 915, 894, 870; ^1H NMR (pyridine-d_5), δ (ppm): 6.32 (1H, brs, 1″-H), 5.39 (1H, brs, 6-H), 4.96 (1H, d, J = 6.4 Hz, 1′-H), 1.76 (3H, d, J = 6.16 Hz, 6″-CH_3), 1.19 (d, J = 6.25 Hz, 21-CH_3, 25*R*), 1.18 (3H, d, J = 6.0 Hz, 21-CH_3, 25*S*), 1.07 (3H, s, 18-CH_3), 0.99 (3H, s, 19-CH_3), 1.08(3H, d, J = 2.10 Hz, 27-CH_3, 25*S*), 0.68 (d, J = 5.50 Hz, 27-CH_3, 25*R*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

2.3.3. 25(R,S)-Dracaenoside G (7)

White amorphous powder, $C_{45}H_{72}O_{17}$, $[\alpha]_D^{20}$ − 102.63° (MeOH, $c = 0.2$). Negative ion HRFAB-MS, *m/z*: 883.4687 $[M - H]^+$ (calcd. 883.4691). Negative ion FAB-MS, *m/z*: 883 $[M - H]^+$, 737 $[M - 146]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3428

Table 1
^{13}C NMR signals of the aglycon moieties of the dracaenosides **5–22**

Position	**5** (*R*/*S*)	**6** (*R*/*S*)	**7** (*R*/*S*)	**8** (*R*/*S*)	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19** (*R*/*S*)	**20** (*R*/*S*)	**21**	**22**
1	37.5	37.6	37.6	37.6	37.5	37.6	37.5	37.637.8	37.5	37.9	37.7	37.6	37.5	37.2	37.3	37.2	37.3	
2	30.3	30.1	30.1	30.2	30.1	30.2	30.3	30.1	30.2	30.2	30.3	30.3	30.4	30.2	30.3	30.2	30.2	30.3
3	78.2	78.3	78.3	77.9	78.5	78.5	78.2	78.5	78.6	78.3	78.2	78.6	78.6	78.1	78.5	78.7	78.6	78.7
4	39.4	39.1	39.1	38.8	38.8	39.4	39.1	39.9	40.0	40.0	39.1	39.9	39.2	39.0	39.0	38.8	39.0	38.8
5	140.5	140.4	140.5	140.4	140.8	140.3	140.4	140.3	140.4	140.3	140.4	140.5	140.4	140.4	140.9	140.9	140.9	140.9
6	122.5	122.5	122.5	122.6	121.9	122.5	122.4	122.5	122.4	122.4	122.6	122.7	122.6	122.4	121.9	122.0	122.0	122.0
7	26.8	26.8	26.9	26.8	32.2	26.8	26.7	26.8	26.7	26.7	26.9	26.9	26.9	26.7	32.3	32.5	32.4	32.5
8	35.7	35.7	35.8	35.8	31.8	35.7	35.7	35.7	35.7	35.5	35.8	35.8	35.2	35.6	31.7	31.8	31.7	31.8
9	43.7	43.7	43.7	43.7	50.3	43.7	43.7	43.6	43.7	43.7	43.8	43.8	43.8	43.7	50.4	50.5	50.4	50.5
10	37.8	37.8	37.9	37.8	37.2	37.8	37.8	37.8	37.8	37.9	37.9	37.9	37.8	37.8	37.6	37.6	37.5	37.6
11	20.5	20.5	20.5	20.5	21.2	20.5	20.4	20.5	20.4	20.4	20.5	20.6	20.7	20.4	21.1	21.2	21.1	21.2
12	32.1	32.0	32.1	32.1	39.9	32.0	29.9	31.9	31.9	31.8	30.7	32.0	32.1	31.9	39.9	40.0	39.8	40.0
13	45.2	45.3	45.2	45.2	40.6	45.2	45.1	45.1	45.5	45.2	45.6	45.7	48.1	45.2	40.5	40.9	40.8	40.9
14	86.5	86.6	86.6	86.6	56.7	86.5	86.5	86.5	86.4	86.2	86.5	86.6	85.6	86.3	56.7	56.7	56.6	56.7
15	39.9	40.0	40.0	40.0	32.4	39.9	39.9	38.8	39.0	39.0	40.2	38.9	42.6	39.9	32.2	32.6	32.4	32.6
16	82.0	82.1	82.1	82.0	81.5	82.0	82.4	82.4	82.2	82.2	81.9	82.0	85.0	82.0	81.2	81.3	81.4	81.3
	82.1	82.2	82.2	82.1											81.5	81.5		
17	60.0	60.0	60.0	59.9	62.9	59.9	59.5	59.5	60.1	60.1	60.7	60.8	62.2	59.7	62.9	62.9	64.2	63.9
	59.9	59.9	59.9	59.8											62.8	62.8		
18	20.2	20.1	20.2	20.1	16.4	20.1	19.9	20.1	20.3	18.7	20.3	20.4	18.1	19.9	16.4	16.6	16.3	16.6
19	19.4	19.5	19.5	19.5	19.5	19.4	19.4	19.4	19.5	19.4	19.5	19.6	19.6	19.4	19.5	19.6	19.5	19.6
20	42.6	42.6	42.6	42.2	41.9	39.2	42.7	42.7	40.1	40.1	40.9	40.9	105.3	38.7	42.0	42.0	40.8	40.9
	42.0	42.4	42.4	42.7											42.5	42.4		
21	15.5	15.5	15.4	15.5	15.1	15.4	15.2	15.3	16.7	16.7	16.9	16.9	12.1	15.6	15.1	15.1	16.4	16.6
	15.3	15.4	15.4	15.3											15.0	15.0		
22	109.9	109.7	109.8	109.7	109.5	110.1	111.8	111.9	110.3	110.3	111.2	111.3	154.4	120.9	109.3	109.4	110.9	110.9
	110.2	110.2	110.3	110.2											109.8	109.7		
23	32.1	32.1	32.1	32.05	33.3	26.8	36.3	36.2	31.2	31.0	32.1	32.2	31.9	33.9	31.9	30.2	30.2	30.2
	27.7	27.7	27.7	26.69											26.5	26.6		
24	29.4	29.5	29.5	29.46	29.0	24.2	66.6	66.6	27.7	27.7	28.5	28.6	26.9	28.8	29.3	28.4	28.2	28.4
	26.7	26.7	26.7	26.38											26.3	26.4		
25	30.7	30.1	30.1	30.72	144.5	42.2	35.9	35.9	34.5	34.3	34.6	34.5	31.2	88.4	30.7	30.6	34.5	34.5
	26.4	26.4	26.4	27.67											27.6	27.5		
26	66.9	66.9	67.0	66.96	65.0	64.5	64.6	64.6	75.3	75.3	75.3	75.1	75.3	66.9	66.9	66.8	75.3	75.4
	65.2	65.2	65.2	65.21											65.1	65.0		
27	17.45	17.5	17.5	17.46	108.8	64.1	9.8	9.8	17.7	17.6	17.7	17.7	17.9	65.4	17.4	17.5	17.6	17.6
	16.43	16.5	16.4	16.45											16.4	16.3		

Table 2
^{13}C NMR signals of the sugar moieties of the saponins **5**–**22** (in C_5D_5N)

Position	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Glc-1	102.4	100.4	100.3	99.9	100.0	99.9	100.3	99.9	102.1	100.3	100.3	100.0	100.3	100.2	100.3	99.8	100.4	100.0
2	75.6	78.3	78.1	77.2	78.7	78.5	78.9	78.5	75.3	78.3	78.7	78.8	78.8	78.6	78.2	78.5	78.6	78.5
3	76.8	79.7	76.9	89.5	89.5	89.5	77.9	89.5	77.0	79.7	78.0	89.4	89.4	77.9	77.9	89.4	77.8	77.8
4	78.4	71.9	77.9	69.7	69.7	77.1	78.0	77.1	78.3	71.8	78.2	77.3	77.0	78.0	78.7	77.0	78.1	78.6
5	77.1	78.6	78.0	77.8	77.9	78.8	76.9	78.7	77.9	78.7	77.0	77.9	78.1	77.0	76.9	78.7	76.9	77.2
6	61.6	62.8	61.3	62.5	62.5	62.5	61.4	62.5	61.2	61.3	61.4	62.6	61.5	61.3	61.3	62.4	61.3	62.5
Rha-1		102.2	102.1	102.3	102.3	102.3	102.0	102.3		102.2	102.1	102.3	102.2	102.1	102.1	102.2	102.2	102.3
2		72.7	72.6	72.5	72.5	72.5	72.5	72.5		72.8	72.6	72.6	72.7	72.6	72.6	72.5	72.6	72.5
3		72.9	72.8	72.9	72.8	72.8	72.8	72.8		72.9	72.8	72.9	72.9	72.8	72.8	72.8	72.8	72.9
4		74.2	74.2	74.2	74.1	74.2	74.2	74.1		74.2	74.2	74.2	74.2	74.2	73.9	74.1	74.2	74.2
5		69.6	69.6	69.7	69.7	69.6	69.5	69.7		69.6	69.6	69.8	69.7	70.0	69.6	69.6	69.6	69.7
6		18.8	18.7	18.8	18.8	18.8	18.7	18.8		18.7	18.6	18.9	18.7	18.6	18.7	18.7	18.7	18.8
Glc′-1				104.6	104.6	104.6		104.6				104.6	104.9			104.6		104.9
2				75.0	75.0	75.0		75.0				75.1	75.3			75.0		75.0
3				78.5	77.1	77.8		77.6				78.6	78.6			77.7		77.2
4				71.6	71.5	71.6		71.5				71.9	71.8			71.5		71.6
5				78.7	77.7	77.9		77.9				78.6	78.7			77.9		77.8
6				62.5	62.4	62.5		62.5				62.6	62.9			62.4		62.5
Rha′-1	102.8		102.9				102.9		102.9		102.9			102.9	102.9		103.0	
2	72.7		72.6				72.5		72.6		72.6			72.6	72.6		72.6	
3	72.9		72.9				72.9		72.8		72.9			72.9	72.9		72.9	
4	74.1		73.9				73.9		74.0		74.0			74.0	74.1		73.9	
5	70.4		70.5				70.5		70.5		70.5			70.5	70.5		70.5	
6	18.6		18.6				18.5		18.5		18.8			18.7	18.6		18.6	
Glc″-1									105.1	105.1	105.0	105.0	105.1				105.1	105.2
2									75.3	75.3	75.3	75.3	75.1				75.0	75.3
3									78.7	78.7	78.7	78.7	78.7				78.7	78.6
4									71.8	71.8	71.8	71.8	71.8				71.8	71.7
5									78.6	78.6	78.6	78.5	78.6				78.6	78.5
6									62.7	62.9	62.9	62.9	62.9				62.9	62.9

(br, OH), 2940 (CH), 2868 (CH), 1645, 917, 898, 878; ^{1}H NMR (pyridine-d_5), δ (ppm): 6.34 (1H, brs, 1″-H), 5.81 (1H, brs, 1‴-H), 5.38 (1H, brs, 6-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.74 (3H, d, J = 5.55 Hz, 6″-CH_3), 1.59 (3H, d, J = 5.40 Hz, 6‴-CH_3), 1.17 (1H, d, J = 5.56 Hz, 21-CH_3), 1.16 (1H, d, J = 5.56 Hz, 21-CH_3), 1.11 (3H, s, 18-CH_3), 1.06 (3H, s, 19-CH_3), 1.06 (3H, brs, 27-CH_3, 25*S*), 0.68 (3H, brs, 27-CH_3, 25*R*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

2.3.4. 25(R,S)-Dracaenoside H (**8**)

Amorphous solid, $C_{45}H_{72}O_{18}$, $[\alpha]_D^{20}$ − 69.77° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m*/*z*: 899.4681 $[M - H]^-$ (calcd. 899.4640). Negative ion FAB-MS, *m*/*z*: 900 $[M]^+$, 737 $[M - 162 - H]^-$, 754 $[M - 146]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3424 (br, OH), 2943 (CH), 2337, 1652, 1050, 920, 897. ^{1}H NMR (pyridine-d_5, 400 MHz), δ (ppm): 6.39 (1H, brs, 1″-H), 5.40 (1H, brs, 6-H), 5.07 (1H, d, J = 7.76, 1‴-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.74 (3H, d, J = 5.55 Hz, 6″-CH_3), 1.17 (1H, d, J = 5.56 Hz, 21-CH_3, 25*S*), 1.19 (1H, d, J = 5.56 Hz, 21-CH_3, 25*R*), 1.12 (3H, s, 18-CH_3), 1.06 (3H, s, 19-CH_3), 0.66 (brs, 27-CH_3, 25*R*), 1.07 (brs, 27-CH_3, 25*S*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

2.3.5. Dracaenoside I (**9**)

Amorphous solid, $C_{45}H_{70}O_{17}$, $[\alpha]_D^{20}$ − 62.50° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m*/*z*: 881.4500 $[M - H]^-$ (calcd. 881.4534). Negative ion FAB-MS, *m*/*z*: 881 $[M - H]^-$, 719 $[M - 162 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3428 (br, OH), 2937 (CH), 2904, 1652, 1048, 920; ^{1}H NMR (pyridine-d_5), δ (ppm): 6.35 (1H, brs, 1″-H), 5.48 (1H, brs, 27-H), 5.34 (1H, brs, 6-H), 5.09 (1H, brs, 27-H), 5.08 (1H, d, J = 7.76 Hz, 1‴-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.11 (3H, d, J = 6.8 Hz, 21-CH_3), 1.09 (3H, s, 18-CH_3), 1.06 (3H, s, 19-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

2.3.6. Dracaenoside J (**10**)

Amorphous solid, $C_{45}H_{72}O_{19}$, $[\alpha]_D^{20}$ − 85.00° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m*/*z*: 915.4572 $[M - H]^+$ (calcd. 915.4589). Negative ion FAB-MS, *m*/*z*: 915 $[M - H]^-$, 769 $[M - 146 - H]^-$, 753 $[M - 162 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3428 (br, OH), 2935 (CH), 1652. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.39 (1H, brs, 1″-H), 5.39 (1H, brs, 6-H), 5.08 (1H, d, J = 7.76 Hz, 1‴-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.18 (3H, d, J = 6.80 Hz, 21-CH_3), 1.12 (3H, s, 18-CH_3),

0.99 (3H, s, 19-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.7. Dracaenoside K (**11**)*

White amorphous powder, $C_{45}H_{72}O_{18}$, $[\alpha]_D^{20}$ − 100.00° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 899.4678 $[M - H]^-$ (calcd. 899.4640). Negative ion FAB-MS, *m/z*: 900 $[M]^+$, 753 $[M - 146 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3434 (br, OH), 2931 (CH), 1635. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.35 (1H, brs, 1″-H), 5.08 (1H, brs, 1‴-H), 5.39 (1H, brs, 6-H), 4.91 (1H, d, J = 6.76 Hz, 1′-H), 3.90 (1H, m, 3-H), 1.75 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.30 (3H, d, J = 6.96 Hz, 27-CH_3), 1.21 (3H, d, J = 6.84 Hz, 21-CH_3), 1.05 (3H, s, 18-CH_3), 1.11 (3H, s, 19-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.8. Dracaenoside L (**12**)*

White amorphous powder, $C_{45}H_{72}O_{19}$, $[\alpha]_D^{28}$ − 66.67° (MeOH, c = 0.2). Negative ion FAB-MS, *m/z*: 915 $[M - H]^-$, 753 $[M - 162 - H]^-$, 769 $[M - 146 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3434 (br, OH), 2931 (CH), 1635. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.35 (1H, brs, 1″-H), 5.08 (1H, d, J = 7.56 Hz, 1‴-H), 5.39 (1H, brs, 6-H), 4.91 (1H, d, J = 6.76 Hz, 1′-H), 3.90 (1H, m, 3-H), 1.75 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.30 (3H, d, J = 6.84 Hz, 27-CH_3), 1.21 (3H, d, J = 6.84 Hz, 21-CH_3), 1.05 (3H, s, 18-CH_3), 1.12 (3H, s, 19-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.9. 25(R,S)-Dracaenoside M (**13**)*

Amorphous solid, $C_{45}H_{74}O_{19}$, $[\alpha]_D^{20}$ − 74.90° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 917.4753 $[M - H]^+$ (calcd. 917.4746). Negative ion FAB-MS, *m/z*: 932 $[M + 14]^+$, 769 $[M + 14 - 146 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3428 (br, OH), 2935 (CH), 1652. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.39 (1H, brs, 1″-H), 5.39 (1H, brs, 6-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 4.81 (1H, d, J = 7.76, 1‴-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.18 (3H, d, J = 6.80 Hz, 21-CH_3), 1.12 (3H, s, 18-CH_3), 0.99 (3H, s, 19-CH_3), 1.01 (3H, d, J = 7.44 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Enzymatic hydrolysis of 25-(R,S)-dracaenoside M. 25(*R*, *S*)-Dracaenoside M (5 mg) was treated with β-glucosidase (10 mg) in HOAc–NaOAC buffer (pH 5, 5 ml) at room temperature for 12 h to obtain **5**.

*2.3.10. Mixture of ophipojaponin A and 25(S)-dracaenoside N (**14**)*

Amorphous solid, $C_{45}H_{74}O_{19}$, $[\alpha]_D^{20}$ − 74.90° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 917.4754 $[M - H]^+$ (calcd. 917.4746). Negative ion FAB-MS, *m/z*: 932 $[M + 14]^+$, 769 $[M + 14 - 146 - H]^-$. IR, ν_{max}^{KBr} (cm^{-1}): 3428 (br, OH), 2935 (CH), 1652. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.39 (1H, brs, 1″-H), 5.39 (1H, brs, 6-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 4.81 (1H, d, J = 7.76, 1‴-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.18 (3H, d, J = 6.80 Hz, 21-CH_3), 1.12 (3H, s, 18-CH_3), 0.99 (3H, s, 19-CH_3), 1.01 (3H, d, J = 7.44 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Enzymatic hydrolysis of mixture of ophipojaponin A and 25(S)-dracaenoside N. Mixture of ophipojaponin A and 25(*S*)-dracaenoside N (5 mg) was treated with β-glucosidase (10 mg) in HOAc–NaOAC buffer (pH 5, 5 ml) at room temperature for 12 h to obtain **6**.

*2.3.11. 25(R,S)-Dracaenoside O (**15**)*

Amorphous solid, $C_{51}H_{84}O_{23}$, $[\alpha]_D^{20}$ − 0.08° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 1063.5337 $[M - H]^+$ (calcd. 1063.5325). Negative ion FAB-MS, *m/z*: 1064 $[M]^+$, 918 $[M - 146]^+$, 772 $[M - 146 - 146]^+$, 610 $[M - 146 - 146 - 162]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3431 (br, OH), 2935 (CH), 1651. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.38 (1H, brs, 1″-H), 5.84 (1H, brs, 1‴-H), 5.41 (1H, brs, 6-H), 4.91 (1H, d, J = 6.0 Hz, 1′-H), 4.83 (1H, d, J = 7.76, 1⁗-H), 1.77 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.62 (3H, d, J = 6.0 Hz, 6′-CH_3), 1.36 (3H, d, J = 7.0 Hz, 21-CH_3), 1.14 (3H, s, 18-CH_3), 1.13 (3H, s, 19-CH_3), 1.01 (3H, d, J = 7.44 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Enzymatic hydrolysis of 25-(R,S)-dracaenoside O. 25(*R*, *S*)-Dracaenoside O (2 mg) was treated with β-glucosidase (4 mg) in HOAc–NaOAC buffer (pH 5, 3 ml) at room temperature for 12 h to afford **7** and glucose.

*2.3.12. 25(R,S)-Dracaenoside P (**16**)*

Amorphous solid, $C_{51}H_{84}O_{24}$, $[\alpha]_D^{20}$ − 45.00° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 1079.5211 $[M - H]^+$ (calcd. 1079.5274). Negative ion FAB-MS, *m/z*: 1080 $[M]^+$, 918 $[M-162]^+$, 756 $[M-162-162-H]^+$, 610 $[M - 162 - 146 - 162]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3424 (br, OH), 2930 (CH), 1647. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.35 (1H, brs, 1″-H), 5.85 (1H, brs, 1‴-H), 5.34 (1H, brs, 6-H), 5.08 (1H, brs, 27-H), 5.08 (1H, d, J = 7.76 Hz, 1⁗-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.35 (3H, d, J = 7.85 Hz, 21-CH_3), 1.13 (3H, s, 18-CH_3), 1.11 (3H, s, 19-CH_3), 1.02 (3H, d, J = 6.50 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

Enzymatic hydrolysis of 25-(R,S)-dracaenoside P. 25(*R*, *S*)-Dracaenoside P (2 mg) was treated with β-glucosidase (4 mg) in HOAc–NaOAC buffer (pH 5, 3 ml) at room temperature for 12 h to afford **8** and glucose.

*2.3.13. 25(R,S)-Dracaenoside Q (**17**)*

Amorphous solid, $C_{51}H_{82}O_{23}$, $[\alpha]_D^{20}$ − 65.53° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 1061.5221 $[M - H]^+$ (calcd. 1061.5168). Negative ion FAB-MS, *m/z*: 1062 $[M]^+$, 915 $[M - 146 - H]^+$, 769 $[M - 146 - 162 - H]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3419 (br, OH), 2932 (CH), 1653. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.35 (1H, brs, 1″-H), 5.82 (1H, brs, 1‴-H), 5.34 (1H, brs, 6-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.78 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.74 (3H, s, 21-CH_3), 1.60 (3H, d, J = 6.0 Hz, 6‴-CH_3), 1.08 (3H, s, 18-CH_3), 1.05 (3H, s, 19-CH_3), 1.02 (3H, d, J = 6.50 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.14. Dracaenoside R (**18**)*

Amorphous solid, $C_{45}H_{72}O_{19}$, $[\alpha]_D^{20}$ − 75.13° (MeOH, c = 0.2). Negative ion HRFAB-MS, *m/z*: 915.4513 $[M-H]^+$ (calcd. 915.4589). Negative ion FAB-MS, *m/z*: 915 $[M-H]^+$, 769 $[M-146-H]^+$. IR, ν_{max}^{KBr} (cm^{-1}): 3434 (br, OH), 2937 (CH), 1652. ^{1}H NMR (pyridine-d_5), δ (ppm): 6.38 (1H, brs, 1″-H), 5.84 (1H, brs, 1‴-H), 5.36 (1H, brs, 6-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.76 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.62 (3H, d, J = 6.0 Hz, 6‴-CH_3), 1.16 (3H, d, J = 6.84 Hz, 21-CH_3), 1.11 (3H, s, 18-CH_3), 1.05 (3H, s, 19-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.15. 25(R,S)-Spirost-5-en-3-ol 3-O-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside (mixture of dioscin and collettinside III) (**19**)*

White amorphous powder, $C_{45}H_{72}O_{16}$. Negative ion FAB-MS, *m/z*: 867 $[M-H]^-$, 721 $[M-H-146]^-$. ^{1}H NMR (pyridine-d_5, 500 MHz), δ (ppm): 3.90 (1H, m, H-3), 4.57 (1H, m, H-16), 5.10 (1H, d, J = 7.7 Hz, H-Glc-1), 5.53 (1H, d, J = 6.9 Hz, H-Glc′-1), 6.01 (1H, s, H-Rha-1), 1.79 (3H, d, J = 6.5 Hz, H-Rha-6), 0.81 (3H, s, H-18), 1.05 (3H, s, H-19), 1.13 (3H, d, J = 6.7 Hz, H-21, 25*R*), 1.12 (3H, d, J = 6.7 Hz, H-21, 25*S*), 1.00 (3H, d, J = 6.20 Hz, 27-CH_3, 25*R*), 0.69 (3H, d, J = 9.1 Hz, H-27, 25*S*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.16. 25(R,S)-Spirost-5-en-3-ol 3-O-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside (mixture of gracillin and collettinside IV) (**20**)*

White amorphous powder, $C_{45}H_{72}O_{17}$. Negative ion FAB-MS, *m/z*: 883 $[M-H]^-$, 721 $[M-H-162]^-$. ^{1}H NMR (pyridine-d_5, 500 MHz), δ (ppm): 6.39(1H, brs, 1″-H), 5.34 (1H, brs, 6-H), 5.04 (1H, d, J = 7.76 Hz, 1‴-H), 4.90 (1H, d, J = 6.0 Hz, 1′-H), 1.73 (3H, d, J = 6.0 Hz, 6″-CH_3), 1.18 (1H, d, J = 5.56 Hz, 21-CH_3, 25*R*), 1.17 (1H, d, J = 5.56 Hz, 21-CH_3, 25*S*), 1.12 (3H, s, 18-CH_3), 1.06 (3H, s, 19-CH_3), 1.00 (3H, d, J = 6.20 Hz, 27-CH_3, 25*R*), 0.66 (3H, d, J = 6.20 Hz, 27-CH_3, 25*S*). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.17. 26-O-β-D-Glucopyranosyl 25(R,S)-furost-5-en-3,22ξ,26-triol 3-O-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl(1,3)]-β-D-glucopyranoside (mixture of protodioscin and protoneodioscin) (**21**)*

White amorphous powder, $C_{51}H_{84}O_{22}$. Negative ion FAB-MS, *m/z*: 1048 $[M]^+$, 902 $[M-146]^+$, 756 $[M-146-146]^+$, 594 $[M-146-146-162]^+$. ^{1}H NMR (pyridine-d_5, 500 MHz), δ (ppm): 3.90 (1H, m, H-3), 4.57 (1H, m, H-16), 5.32 (1H, brs, H-6), 5.80 (1H, brs, H-1‴), 6.32 (1H, brs, H-1″), 4.90 (1H, d, J = 6.60 Hz, H-1′), 4.82 (1H, d, J = 6.60 Hz, H-1⁗), 0.87 (3H, s, 18-CH_3), 1.04 (3H, s, 19-CH_3), 1.31 (3H, d, J = 6.35 Hz, 21-CH_3), 1.00 (3H, d, J = 6.20 Hz, 27-CH_3). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.18. 26-O-β-D-Glucopyranosyl 25(R,S)-spirost-5-en-3,22ξ,26-triol 3-O-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside (mixture of protogracillin and protoneogracillin) (**22**)*

White amorphous powder, $C_{51}H_{84}O_{23}$. Negative ion FAB-MS, *m/z*: 1064 $[M]^+$, 901 $[M-162-H]^-$, 755 $[M-162-146-H]^-$, 593 $[M-162-146-162-H]^-$, 432 $[M-162-146-162-162]^+$. ^{1}H NMR (pyridine-d_5, 400 MHz), δ (ppm): 6.33 (1H, brs, H-1″), 5.32 (1H, brs, H-6), 5.08 (1H, d, J = 6.50 Hz, H-1‴), 4.92 (1H, d, J = 6.20 Hz, H-1′), 4.87 (1H, d, J = 6.60 Hz, H-1′), 1.73 (3H, d, J = 5.85 Hz, H-6″), 1.31 (3H, d, J = 6.40 Hz, H-21), 1.05 (3H, s, CH_3-19), 0.88 (3H, s, CH_3-18), 0.99 (3H, d, J = 6.20 Hz, CH_3-27). ^{13}C NMR (pyridine-d_5): see Tables 1 and 2.

*2.3.19. Sugar analysis of compounds **5**–**22***

Each compound (2 mg) in 1 M HCl (dioxane–H_2O, 1:1, 1 ml) was heated at 100 °C for 2 h. After removing the solution under reduced pressure, the residue was extracted with chloroform three times. The monosaccharide fraction was condensed. The residue was dried and solved in pyridine (5 ml). The 0.5 ml trimethylchlorosilane was added into the pyridine solution and reacted 30 min in room temperature. The solution was condensed under reduce pressure; the residue was washed with 0.5 ml ether. The product was analyzed by means of GC–MS. The retention time of L-rhamnose and D-glucose were 7.17 and 11.43 min, respectively.

3. Result and discussion

The fresh stem of *D. cochinchinensis* was extracted with hot methanol. After removal of the solvent under reduced pressure, the residue was partitioned between H_2O and *n*-butanol. The *n*-butanol fraction was supplied to a high porous absorption resin (Diaion HP-20) column chromatography, eluting with H_2O and methanol. The methanol fraction was repeatedly chromatographed on silica gel and octadecylsilanized (ODS) silica gel to afford 18 steroidal saponins (**5**–**22**).

Compounds **19**–**22** were known 25(*R*,*S*)-steroidal saponin epimers, identified as 25(*R*,*S*)-spirost-5-en-3-ol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside (dioscin and collettinside III) (**19**) [7,10], 25(*R*,*S*)-spirost 5-en-3-ol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside (gracillin and collettinside IV) (**20**) [7,10], 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5-en-3,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl(1,3)]-β-D-glucopyranoside (protodioscin and protoneodioscin) (**21**)

[7,11], 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-spirost-5-en-3, 22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside (protogracillin and protoneogracillin) (**22**) [7,11], respectively, by detailed spectral analysis and compared with reference data.

Saponins **5**–**8** were obtained as white amorphous powder. The negative ion HRFABMS determined their molecular formula as $C_{39}H_{62}O_{13}$, $C_{39}H_{62}O_{13}$, $C_{45}H_{72}O_{17}$, and $C_{45}H_{72}O_{18}$, respectively. NMR data due to the ^{1}H and ^{13}C signals around C-25 of their aglycone moieties revealed that **5**–**8** were spirostanol monodesmosides, existed as mixtures of C-25 *R* and *S* epimers. As far as we know, the isolation of a steroidal mixture of C-25 *R* and *S* epimers is very difficult and could not be done by the present chromatographic technique [12]. Thus, their structures were elucidated as C-25 epimeric mixtures.

The NMR spectral features of **5**–**8** were nearly identical to each other, except for the sugar moieties. Comparing the ^{13}C NMR data of their aglycone moiety with those of diosgenin and yamogenin [13], indicated that the aglycone moiety of **5**–**8** had one more hydroxyl group attached at C-14, which let the methine carbon signal of C-14 ($\delta = 56.7$) in diosgenin and yamogenin changed to a quaternary carbon signal at $\delta = 86.6$ in **5**–**8**. Thus, the sapogenin moiety of **5**–**8** was identified as 25(*R*,*S*)-spirost-5-en-3β,14α-diol (prazerigenin A and neoprazerigenin A) [14].

The negative ion FABMS of saponin **5** showed fragment ions at $m/z = 591$ $[M - 146 - H]^-$ and 429 $[M - 146 - 162 - H]^-$, suggested that **5** contained a deoxyhexosyl as terminal unit and a hexosyl as inner unit at the sugar moiety. Acid hydrolysis of **5** with 1 mol/l HCl in dioxane (v/v, 1:1) afforded D-glucose and L-rhamnose as sugar residue. HMBC spectrum showed the correlations of anomeric proton ($\delta = 4.94$ (d, $J = 7.70$ Hz)) of D-glucopyranosyl unit with C-3 ($\delta = 78.2$) of the aglycone, and anomeric proton ($\delta = 5.89$, brs) of L-rhamnopyranosyl unit with C-4 ($\delta = 78.4$) of glucopyranosyl unit, clearly indicated the location of sugar moieties. Therefore, the structure of **5** was determined as 25(*R*,*S*)-spirost-5-en-3β,14α-diol 3-*O*-α-L-rhamnopyranosyl-(1,4)-β-D-glucopyranoside, named 25(*R*,*S*)-dracaenoside E.

The ^{13}C NMR spectral data together with the result of acidic hydrolysis, showed that saponin **6** had similar structure to that of **5**, except for the linkage position of the L-rhamnopyranosyl unit to the D-glucopyranosyl unit, which was determined on the basis of the glycosylation shift effects of the C-2 ($\delta = 79.7$) of D-glucopyranosyl unit comparing with the reference data ($\delta = 75.6$) [13]. Thus, the structure of **6** was established as 25(*R*,*S*)-spirost-5-en-3β,14α-diol 3-*O*-α-L-rhamnopyranosyl-(1,2)-β-D-glucopyranoside, named 25(*R*,*S*)-dracaenoside F.

Acid hydrolysis of **7** also afforded D-glucose and L-rhamnose. The ^{1}H and ^{13}C NMR spectra (pyridine-d_5) indicated that it had a same sugar chain as that in dioscin [7]. Therefore, **7** was characterized as 25(*R*,*S*)-spirost-5-en-3β,14α-diol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside, named 25(*R*,*S*)-dracaenoside G.

The NMR signals due to the sugar moiety of saponin **8** were in good agreement with those of gracillin [7]. Since then, the structure of **8** was formulated as 25-(*R*,*S*)-spirost-5-en-3β,14α-diol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside, named 25(*R*,*S*)-dracaenoside H.

Dracaenoside I (**9**) was obtained as a white amorphous powder, $[\alpha]_D^{20} - 62.50^\circ$ in MeOH. Negative ion HRFABMS gave a quasi-molecular ion peak at $m/z = 881.4500$ ($[M - H]^-$; calcd. 881.4534) corresponding to an empirical molecular formula $C_{45}H_{70}O_{17}$. Acid hydrolysis of **9** gave D-glucose and L-rhamnose by GC analysis. Compared the NMR feature with that of **20** suggested that saponin **9** contained a same sugar chain as **20**, the difference between these two saponins only appeared in F-ring of their aglycons. Compound **9** showed an exomethylene group at $\delta_C = 108.8$ (CH_2) and 144.5 (C), which was ascribed to C-25 and C-27 by compared with the reference data [15]. On the basis of the above evidence, dracaenoside I (**9**) was formulated as spirost-5, 25(27)-dien-3β-ol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D - glucopyranosyl - (1,3)] - β - D-glucopyranoside.

Saponin **10** gave a molecular formula as $C_{45}H_{72}O_{19}$ by negative ion HRFABMS ($m/z = 915.4572$, $[M - H]^+$; calcd. 915.4589) and it had one more oxygen atom than **8**. The ^{13}C NMR feature is quite similar to that of **8** with exceptions of the signals due to the F-ring carbons. In the case of saponin **10**, the C-27 methyl of **8** was substituted to a hydroxymethyl group, which was deduced as *eq* orientation based on the IR characteristic absorptions at 992 and 1018 cm^{-1} [16]. So, **10** was deduced to be a prazerigenin D-glycoside as (25*S*)-spirost-5-en-3β,14α,27-triol (prazerigenin D) 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside, named dracaenoside J.

Dracaenoside K (**11**) was obtained as a white amorphous powder, $[\alpha]_D^{20} - 100.00^\circ$ in MeOH. Negative ion HRFABMS gave a quasi-molecular ion peak at $m/z = 899.4678$ ($[M - H]^-$; calcd. 899.4640) corresponding to an empirical molecular formula $C_{45}H_{72}O_{18}$. The ^{13}C NMR chemical shifts of **11** are closely related to those of **7** with exceptions of the signals due to the F-ring. A hydroxyl group located on C-24 ($\delta = 66.6$) position caused significant down-field shift of the C-27 methyl group ($\delta = 9.76$) by comparing with the reference data [17]. In addition, the 26-H_2 appeared at $\delta = 3.53$ (H_{eq}, brd, $J = 10.4$ Hz) and $\delta = 4.05$ (H_{ax}, 1H, dd, $J = 3.15$, 10.4 Hz). The *J* values implicated that the 25-H was in equatorial orientation. In the NOESY spectrum of **11**, correlation peak of 24-H ($\delta = 4.60$) with 26-H_{ax} indicated the equatorial orientation of C-24 OH. Thus, the structure of dracaenoside K (**11**) was deduced as (24*S*,25*R*)-spirost-5-en-3β,14α,24β-triol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside.

The ^{13}C NMR spectrum of saponin **12** was quite similar to **11** except the sugar moiety, which was identical to that of **8** by comparing their spectral data. Thus, the structure of **12** was deduced as (24*S*,25*R*)-spirost-5-en-3β,14α,24β-triol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside, named dracaenoside L.

25(*R*,*S*)-Dracaenosides M–P (**13**–**16**) were obtained as white amorphous powders. The negative ion HRFABMS determined their molecular formula as $C_{45}H_{74}O_{19}$ for **13** and **14**, $C_{51}H_{84}O_{23}$ for **15**, and $C_{51}H_{84}O_{24}$ for **16**, respectively. The positive color reaction in Ehrlich test and the characteristic ^{13}C NMR signals suggested that all of these four compounds are furostanol glycoside with same aglycon [18]. Enzymatic hydrolysis of **13** and **14** gave **5** and **6**, respectively, together with D-glucose. Therefore, the structures of **13** and **14** were characterized as 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5-en-3β,14α,22ξ,26-tetrol 3-*O*-α-L-rhamnopyranosyl-(1,4)-β-D-glucopyranoside [25(*R*,*S*)-dracaenoside M (**13**)], and 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5-en-3β,14α,22,26-tetrol 3-*O*-α-L-rhamnopyranosyl-(1,2)-β-D-glucopyranoside (**14**), respectively. The 25-(*R*) epimer of **14** was a known saponin once isolated from *Ophipogon japonicus* [19], named ophipojaponin A, and its 25-(*S*)-epimer was given the trivial name of 25(*S*)-dracaenoside N.

Enzymatic hydrolysis of **15** and **16** gave **7** and **8**, respectively, together with D-glucose. Therefore, the structures of **15** and **16** were elucidated as 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5-ene-3β,14α,22ξ,26-tetrol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside [25(*R*,*S*)-dracaenoside O (**15**)], and 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5-en-3β,14α,22ξ,26-tetrol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside [25(*R*,*S*)-dracaenoside P (**16**)], respectively.

The molecular formula $C_{51}H_{82}O_{23}$ was deduced for saponin **17** from its quasi-molecular ion peak at m/z = 1061.5222 (calcd. for $C_{51}H_{82}O_{23}$ 1061.5169) in the HRFABMS. Comparison of the ^{1}H and ^{13}C NMR spectra of **17** with those of compound **16** showed that both structures are very similar except an additional double bond signals at the aglycon of **17**. The downfield chemical shifts of C-22 (δ = 154.4) and C-20 (δ = 105.3) indicated the olefinic substitution located between C-22 and C-20 [20]. Acid hydrolysis of **17** gave L-rhamnose and D-glucose as sugar residue by GC analysis. Therefore, **17** was identified as 26-*O*-β-D-glucopyranosyl 25(*R*,*S*)-furost-5,20(22)-dien-3β,14α,26-triol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[β-D-glucopyranosyl-(1,3)]-β-D-glucopyranoside, named 25(*R*,*S*)-dracaenoside Q.

Saponin **18** was obtained as a white amorphous powder, $[\alpha]_D^{20}$ − 75.13° in MeOH, with a molecular formula $C_{45}H_{72}O_{19}$ (negative ion HRFABMS, m/z = 915.4513 ($[M-H]^-$, calcd. 915.4589)). Acid hydrolysis of **18** gave the D-glucose, L-rhamnose in a ratio 1:2. Comparison the ^{13}C NMR data with those of **7**, suggested that the partial structure rings A–E (C-1–C-21) of **18** was similar to that of **7**. Significant differences were the carbon signals of F-ring. In the spectrum of **18**, the downfield of C-26 and C-27 to δ = 66.9 and 65.4, indicated that these positions were oxygenated. The furospirostane skeleton was deduced from an easily distinguished tertiary carbon signal in δ = 120.9, which was assigned to C-22 [13]. Thus, the structure of dracaenoside *R* (**18**) was determined as furospirost-5-en-3β,14α,26,27-tetrol 3-*O*-α-L-rhamnopyranosyl-(1,2)-[α-L-rhamnopyranosyl-(1,4)]-β-D-glucopyranoside.

It is well known that the C-27 steroidal glycosides were widely distributed in plant kingdom, especially in the families of Liliaceae and Agavaceae [21]. The molecular diversity of steroidal saponins was exhibited not only on the sugar moiety, but also the structure of aglycons. The biological activities and physiological functions of steroidal saponins were dependent on both of their glycosylated level of the sugar moiety and the oxidized level of sapogenins [22]. Generally, the sapogenins occurring in the genus *Dracaena* are characterized with 1,3-dihydroxyl substituents [15,17]. However, most of the saponins isolated from *D. cochinchinensis* were composed of 1,14-dihydroxyl substitutions. It is suggested that as a northernmost species of *Dracaena* in East Asia, *D. cochinchinensis* involved in a specifically secondary metabolism pathway of steroidal saponins. Moreover, it is noticed that the chemical constituents of the fresh stems are quite other with those of the resins. Most compounds isolated from the latter are polyphenols, including chalcones and their oligomers, flavans, flavonoids, stilbenes, as well as lignans. It is proposed that the formation of the red resin may due to a complex physiological, ecological and biochemical process.

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