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Dracaenoside A and B, New C-22 Steroidal Lactone Glycosides from the Stem of *Dracaena cochinchinensis*

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Abstract: Two new C-22 steroidal lactone glycosides, named dracaenoside A and B were isolated from the methanol extract of the fresh stem of *Dracaena cochinchinensis*. Their structures were established as (20S)3β,14α,16β-trihydroxy pregn-5-ene-22-carboxylic acid (22,16)-lactone 3-O-α-L-rhamnopyranosyl (1→2)[α-L-rhamnopyranosyl (1→4)]-β-D-glucopyranoside and (20S)3β, 14α, 16β-trihydroxy pregn-5-ene-22-carboxylic acid (22,16)-lactone 3-O-α-L-rhamnopyranosyl (1→2) [β-D-glucopyranosyl(1→3)]-β-D-glucopyranoside by means of 2D NMR spectral and chemical methods. It is the first time that steroidal lactone glycosides were isolated from the genus *Dracaena*.

Keywords: *Dracaena cochinchinensis*, Agavaceae, C-22 steroidal glycosides, dracaenoside A, dracaenoside B.

The genus *Dracaena* (Agavaceae) consists of about 50 species. In China, the resin of *Dracaena cochinchinensis* S. C. Chen was used as dragon's blood, a traditional medicinal herb. Our previous study on the resins led to the isolation of phenolic compounds together with several C-27 steroidal saponins[1,2,3]. From the fruit of this plant four steroidal saponins were isolated too[4]. In our systematic chemical study on Liliales plants, two new C-22 steroidal lactone glycosides, named as dracaenoside A and B, were isolated from the fresh stem of *D. cochinchinensis*. Their structures were established by means of 2D NMR spectral and chemical methods.

Dracaenoside A was obtained as a white amorphous powder, $[\alpha]_D^{22}$–97.18(c 0.2, pyridine). It showed green color on TLC reacted with anisaldehyde reagent suggested it had a steroidal skeleton. Negative ion HRFABMS gave a quasi molecular peak at 813.3893 ([M-H]$^-$; cal. 813.3908) corresponding to an empirical molecular formula $C_{40}H_{62}O_{17}$. It exhibited a strong IR absorption band at 1750.7 cm^{-1} suggesting the presence of a five-member lactone[5]. The ^{1}H and ^{13}C NMR spectra (pyridine-d_5) of dracaenoside A indicated the presence of three sugar units attributed to the sugar residues and suggested that they were two α-L-rhamnopyranosyl groups [anomeric protons at δ 6.38 (1H, brs) and 5.84 (1H, brs); secondary methyl groups at δ 1.62 (d, 3H, J=6.0Hz) and 1.76 (d, 3H, J=6.1Hz); anomeric carbons at δ 102.94 and 102.10] and a

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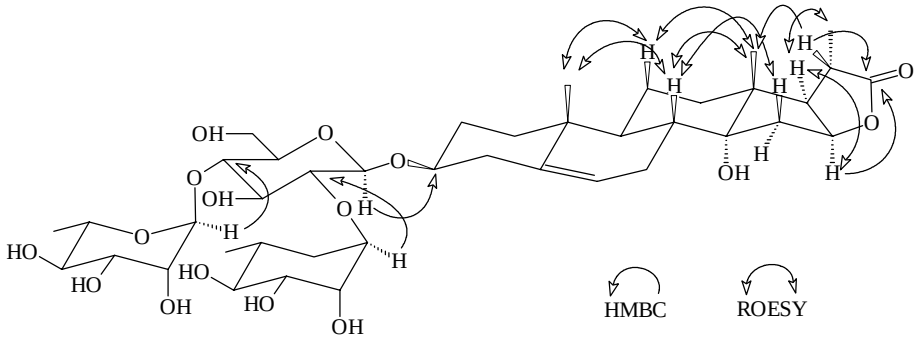
β-D-glucopyranosyl group [anomeric proton at δ 4.91 (d, 1H, J=6.0Hz); anomeric carbon at δ 100.27]. Besides of sugar moieties, there are 22 carbon peaks appeared at ^{13}C NMR spectrum. Two tertiary methyl groups at δ 17.15 [δ 0.93, s, 3H] and 19.37[1.07, s, 3H] and one secondary methyl group at δ 18.52 [δ 1.26 (d, 3H, J=6.0Hz)] were assigned to C-18, C-19 and C-21 of steroidal skeleton. The presence of the oxygenic groups at C-3, C-14 and C-16 at δ 77.86(C-3), 84.16(C-14) and 83.54 (C-16) was assigned in comparison with literatural data[6]. An olefinic proton at δ 5.36 (brs, 1H) suggested a double band on the C-5, which was deduced by downfield shift of the tertiary methyl group (C-19) at δ 19.37. The correlation peaks in HMBC between signals of δ 181.83 and the proton signals at H-20 (δ 2.75) and H-16 (δ 5.34) indicated the location of the carboxylic carbon (δ 181.83) at C-22. The conformation of the aglycone was ascertained by the ROESY correlations observed between H-8 and H-19, H-8 and H-18, H-8 and H-15β[δ1.93, dd, J=14.50, 3.50Hz], H-18 and H-20, respectively. It indicated the ring junctions should be B/C trans, C/D trans and D/E cis. The correlations between H-17 and H-21, H-17 and H-16 indicated the α-orientation of 21-CH_3. The orientation of C-3 β-hydroxyl group was confirmed by the ROESY observed between H-3 and H-1eq, H-3 and H-4eq.

Figure 1 Selected HMBC and ROESY correlations of dracaenoside A



Assignment of the sugar moieties was performed by the ^1H-^1H COSY and HMQC-TOCSY spectra combined with HMBC spectrum. Starting from the easily distinguished anomeric protons, it led to the total assignment of each carbon signal by means of HMQC-TOCSY spectra. Detail inspection of HMBC spectrum led to the determination of conjunction of sugar chain. A cross peak between the anomeric proton of inner β-D-glucopyranosyl unit (δ_H 4.91) and C-3 position (δ 77.86) of the aglycone indicated the inner glucose unit was linked to C-3 position. Two terminal α-L-rhamnopyranosyl units were linked on the C′-2 (a cross peak between δ_H 6.38 and δ_C 78.61) and C′-4 (a cross peak between δ_H 5.84 and δ_C 77.98) of β-D-glucopyranosyl unit. The conformations of sugars were determined by GC-MS after trimethylsilanization compared with standard sugars (retention time for L-rhamnose at 7.17 min, D-glucose at 11.43 min).

Acid hydrolysis of dracaenoside A in 1 mol/L HCl (dioxane-H_2O, 1:1, 1 mL) gave the monosaccharides residue. The monosaccharide residue was conducted on GC-MS

analysis after trimethylsilanization. The sugar units were determined as L-rhamnose (R*t*, 7.17 min) and D-glucose(R*t*, 11.43 min) respectively.

All of these results led to the total assignment of ^{13}C NMR chemical shifts. The structure of this new glycoside was elucidated as (20S)3β, 14α, 16β-trihydroxy pregn-5-ene-22-carboxylic acid (22,16)-lactone 3-O-α-L-rhamnopyranosyl (1→2)[α-L- rhamnopyranosyl (1→4)]-β-D-glucopyranoside.

Table 1 ^{13}C-NMR data of compounds dracaenoside A and B (100MHz. in pyridine-d_5)

	A	B	A		B	
1	37.44	37.42	Glc(inner)		Glc(inner)	
2	30.22	30.09	1’	100.27		99.88
3	77.86	78.54	2’	78.61		77.54
4	39.04	38.69	3’	75.98		89.53
5	140.41	140.35	4’	77.98		69.59
6	122.15	122.16	5’	77.98		78.75
7	26.59	26.57	6’	61.32		62.44
8	43.68	43.68	Rha		Rha	
9	35.06	35.03	1’’	102.10		102.26
10	37.77	37.72	2’’	72.60		72.53
11	19.90	19.89	3’’	72.79		72.83
12	30.35	30.31	4’’	74.17		74.15
13	46.05	46.37	5’’	69.91		69.65
14	84.16	84.12	6’’	18.72		18.75
15	41.72	41.70	Rha		Glc	
16	83.54	83.49	1’’’	102.94		104.59
17	55.53	55.49	2’’’	72.60		74.98
18	17.15	17.11	3’’’	72.89		77.01
19	19.37	19.33	4’’’	73.96		71.52
20	36.50	36.46	5’’’	70.48		77.93
21	18.52	18.48	6’’’	18.52		62.44
22	181.83	181.76				

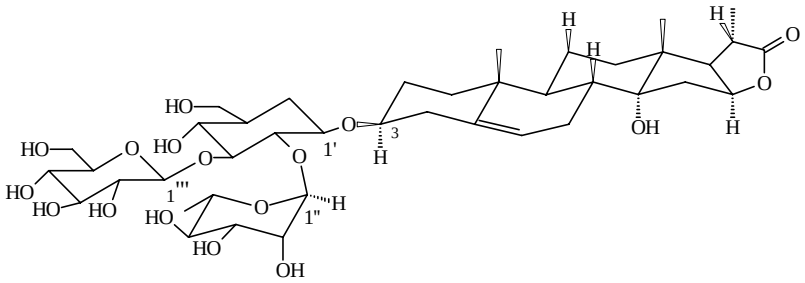
Dracaenoside B was obtained as a white amorphous powder, $[\alpha]_D^{22}$0.0(c 0.2, MeOH). Negative ion HRFABMS gave a quasi molecular peak at 829.3863 ([M-H]$^-$; cal. 829.3857) corresponding to an empirical molecular formula $C_{40}H_{62}O_{18}$. The ^{13}C and ^1H-NMR spectra of dracaenoside B showed it was very similar with that of dracaenoside A and possessed an identical aglycone. The different only appeared in the sugar moieties. Compared with dracaenoside A, which contained two α-L-rhamnopyranosyl units and one β-D-glucopyranosyl unit, dracaenoside B contained two β-D-glucopyranosyl units and one α-L-rhamnopyranosyl unit, which anomeric carbons were observed at δ 99.87, 104.59 and 102.25, secondary methyl groups at δ 1.62 (d, 3H, J=6.0Hz) and 1.76 (d, 3H, J=6.1Hz). It was also confirmed by GC-MS. Compared with the NMR data of dracaenoside A, the α-L-rhamnopyranosyl unit was deduced to be linked on the C-2’ position of the inner glucose. The terminal β-D-glucopyranosyl unit was deduced to be linked on the C-3’ position of the inner β-D-glucopyranosyl unit by its significant downfield shift to 89.53. The total ^{13}C NMR assignment of the sugar moieties was ascertained by comparison with the chemical shifts of reference data[4,6].

The structure of the compound was established as (20S)3β, 14α, 16β-trihydroxy-

pregn-5-ene-22-carboxylic acid (22,16)-lactone 3-O-α-L-rhamnopyranosyl (1→2) [β-D-glucopyranosyl(1→3)]-β-D-glucopyranoside .

Dracaenoside A and B are the first examples that C-22 steroidal lactone glycosides were isolated from the family Agavaceae.

Figure 2 Chemical structure of dracaenoside B



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