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STUDY OF *DRACAENA ANGUSTIFOLIA*

I - NEW SPIROSTANOL SAPOGENINS FROM ROOTS AND RHIZOMES

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SUMMARY

The MeOH extract of Nam ginseng (roots and rhizomes of *Dracaena angustifolia*) afforded three new spirostanol sapogenins, named namogenins A-C (**1**-**3**). Their structures were determined on basis of spectral analyses and chemical methods.

I. INTRODUCTION

Dracaena angustifolia Roxb. (Dracaenaceae) is locally known as Nam ginseng (ginseng from the South) in Quang Nam province. Its underground parts are used as tonic and for treatment of leukemia.[1]

In our continuing studies on Vietnamese medicinal plants, we have examined the constituents of Nam ginseng (D. angustifolia) and isolated three new spirostanol sapogenins. This paper reports the isolation and structure elucidation of these new compounds.

II. RESULTS AND DISCUSSION

Air-dried roots and rhizomes of *D. angustifolia* were extracted successively by refluxing MeOH, 50% aqueous MeOH and water to give MeOH, MeOH-H_2O and H_2O extracts, respectively. The MeOH extract was subjected to Diaion HP-20 column chromatography (CC). The MeOH eluate was further separated by a combination of silica gel and ODS column chromatographies, and normal- and reversed-phase pTLC, to afford three new compounds, named namogenins A-C (**1**-**3**).

Negative-ion HRFABMS of **1** displayed a quasi-molecular ion at *m*/*z* 461.2859, indicating the molecular formula $C_{27}H_{42}O_6$. The ^{1}H NMR spectrum of **1** showed signals ascribable to two tertiary methyls and three secondary methyls, while the ^{13}C NMR spectrum of **1** showed thirty-five signals (Table 1). Analysis of the COSY and HMQC spectra, together with the molecular formula, suggested **1** to be a spirostane-type steroid, but the ^{1}H and ^{13}C NMR signals ascribable to ring F appeared as pairs of signals, indicating that **1** was a C-25 epimeric mixture. Since its isolation was very difficult, as reported for similar epimeric mixtures,[2] and could not be done, the structure of **1** was elucidated by spectroscopic analysis of the epimeric mixture.

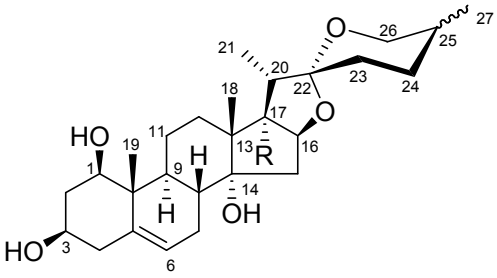
Table 1. ^{13}C NMR Data (□) for Compounds **1**-**3** in Pyridine-d_5.

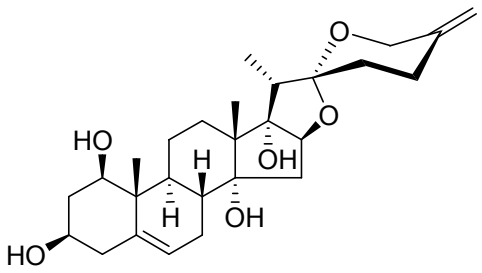
	1		**2**	**3**
1	78.2		78.2	78.2
2	43.6		43.6	43.7
3	68.1		68.1	69.1
4	44.0		44.0	44.1
5	139.8		139.8	139.8
6	124.9		125.0	124.9
7	26.4		26.9	26.4
8	37.5		36.8	37.5
9	44.4		44.5	44.4
10	43.9		43.9	43.9
11	23.2		23.6	23.2
12	27.2		32.7	27.2
13	48.1		44.8	48.2
14	88.2		86.8	88.3
15	40.6		40.1	40.6
16	90.5		81.9	90.8
17	91.2		59.9	91.2
18	21.0		20.4	21.0
19	14.0		13.9	14.0
20	45.2[a]	45.7[b]	42.5	45.1
21	9.9[a]	9.5[b]	15.2	9.9
22	109.6[a]	110.0[b]	110.0	109.8

23	32.2[a]	26.7[b]	26.5	33.6
24	28.9[a]	25.8[b]	26.3	28.7
25	30.4[a]	27.4[b]	27.6	144.2
26	66.8[a]	65.0[b]	65.0	64.9
27	17.3[a]	16.3[b]	16.3	108.8

[a,b] Data for the 25*R*- and 25*S*-epimers, respectively.

Analysis of the COSY and HMQC spectra indicated the disappearance of the methine carbons assignable to C-14 and C-17, but instead of them, ^{13}C NMR spectrum showed signals of two quaternary carbons at 88.2 and 91.2. Thus, C-14 and C-17 seemed to have hydroxyl groups, which were confirmed by the HMBC correlations of H_3-21 and H-16 with the quaternary carbon at 91.2 (C-17) and of H_3-18 with both quaternary carbons at 91.2 (C-17) and 88.2 (C-14). The -orientation of 14-OH and 17-OH was deduced by a comparison of the ^{13}C NMR data with that of (25*R*)-spirost-5-en-3,14,17-triol (ophiogenin).[3] Thus, **1** was determined to be a mixture (1:1) of (25*R*)- and (25*S*)-spirost-5-en-1,3,14,17-tetrol, which were named as (25*R*)- and (25*S*)-namogenin A, respectively.





1 R = OH, 25*R,S*
2 R = H, 25*S*

3

Negative-ion HRFABMS of **2** indicated the molecular formula $C_{27}H_{42}O_5$, one oxygen atom less than **1**. The ^{1}H and ^{13}C NMR spectra of **2** were similar to those of **1**, indicating **2** also to be a spirostane-type steroid. However, the signals ascribable to ring F protons and carbons appeared as only one set, and the chemical shifts of H_3-27 (1.06) and of C-23 to C-27 (Table 1) suggested **2** to be a 25*S*-spirostane-type steroid.[4,5] The ^{13}C NMR spectrum of **2** revealed a highfield shift (59.9) of the oxygenated quaternary carbon assigned to C-17 in **1**. Thus, C-17 was considered to be a methine group, which was confirmed by the ^{1}H-^{1}H connectivity deduced by the analysis of the COSY and HMQC spectra and the HMBC correlations of the methine carbon at 59.9 (C-17) with H_3-21 (1.17), H_3-18 (1.18) and H-16 (5.10) and of the quaternary carbon at 86.8 (C-14) with H_3-18 (

1.18). Thus, namogenin B was determined to be (25*S*)-spirost-5-en-1□,3□,14□-triol (**2**).

The molecular formula of namogenin C (**3**) was determined by negative-ion HRFABMS to be $C_{27}H_{40}O_6$, two hydrogen atoms less than **1**. The ^1H and ^{13}C NMR spectra of **3** were almost the same as those of **1** (Table 1), except for the appearance of signals for an exo-olefin (δ_H 4.79, 2H; δ_C 144.2, 108.8) and the disappearance of the signals of a secondary methyl (CH_3-27) and a methine (CH-25). Thus, **3** was considered to be a 25,27-dehydro derivative of **1**, which was supported by the HMBC correlations of the exo-olefinic protons (□ 4.79, H_2-27) with C-24 (□ 28.7) and C-26 (□ 64.9). Thus, namogenin C was determined to be spirosta-5,25(27)-dien-1□,3□,14□,17□-tetrol (**3**).

III. EXPERIMENTAL SECTION

General Experimental Procedures. Optical rotations were measured on a JASCO DIP-140 digital polarimeter at 25 °C. NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in pyridine-d_5, using TMS as an internal reference. FABMS and HRFABMS was performed using a JEOL JMS-700T mass spectrometer and glycerol was used as matrix.

Plant Material. Nam ginseng (roots and rhizomes of *D. angustifolia*) were collected in Quangnam Province, Vietnam, in November 1998.

Extraction and Isolation. Air-dried roots and rhizomes of *D. angustifolia* (440 g) were extracted by refluxing with MeOH, MeOH-H_2O and H_2O successively to give MeOH (78 g), MeOH-H_2O (77 g) and H_2O (5.5 g) extracts, respectively. Part of the MeOH extract (70 g) was subjected to Diaion HP-20 CC and eluted with H_2O and then MeOH to give a MeOH fraction (7.2 g). The MeOH fraction was then chromatographed on silica gel with $CHCl_3$-MeOH-H_2O (14:6:1) to give 7 fractions. Fraction 1 (1.5 g) was again chromatographed on silica gel to give 3 subfractions. Subfraction 2 (520 mg) was separated on normal- ($CHCl_3$-MeOH-H_2O, 14:6:0.5) and reversed-phase (MeOH-MeCN-H_2O, 2:2:1) pTLC to afford **1** (10 mg), **2** (11.6 mg), **3** (1.6 mg).

A Mixture (1:1) of (25*R*)- and (25*S*)-Namogenin A (1): colorless amorphous solid; $[\alpha]_D^{25}$ –69.2° (*c* 0.6, MeOH); ^1H NMR (C_5D_5N) □ 5.70 (1H, d, *J* = 5.4 Hz, H-6), 4.78 (1H, m, H-16), 4.03 (1H, dd, *J* = 10.1, 2.7 Hz, H-26 of 25*S*-isomer), 3.93 (1H, m, H-3), 3.85 (1H, dd, *J* = 11.7, 4.2 Hz, H-1), 3.49 (2H, m, H_2-26 of 25*R*-isomer), 3.28 (1H, br d, *J* = 10.1 Hz, H-26 of 25*S*-isomer), 2.23 (3H, d, *J* = 7.1 Hz, H_3-21), 1.42 (3H, s, H_3-19), 1.20 (3H, s, H_3-18), 1.06 (3H, d, *J* = 7.1 Hz, H_3-27 of 25*S*-isomer), 0.68 (3H, d, *J* = 5.4 Hz, H_3-27 of 25*R*-isomer); ^{13}C NMR, see Table 1; FABMS *m/z*

461.3 [M-H]$^-$; HRFABMS *m/z* 461.2859 (calcd for [M-H]$^-$ 461.2904).

Namogenin B (2): colorless amorphous solid; $[\alpha]_D^{25}$ –74.5° (*c* 0.8, MeOH); ^{1}H NMR (C_5D_5N) 5.71 (1H, d, *J* = 5.5 Hz, H-6), 5.10 (1H, m, H-16), 4.05 (1H, dd, *J* = 10.8, 2.6 Hz, H-26), 3.33 (1H, br d, *J* = 10.8 Hz, H-26), 3.92 (1H, m, H-3), 3.84 (1H, dd, *J* = 11.5, 4.0 Hz, H-1), 2.82 (1H, m, H-17), 1.43 (3H, s, H_3-19), 1.18 (3H, s, H_3-18), 1.17 (3H, d, *J* = 7.2 Hz, H_3-21), 1.06 (3H, d, *J* = 7.0 Hz, H_3-27); ^{13}C NMR, see Table 1; FABMS *m/z* 445.3 [M-H]$^-$; HRFABMS *m/z* 445.2956 (calcd for [M-H]$^-$ 445.2954).

Namogenin C (3): colorless amorphous solid; $[\alpha]_D^{25}$ –29.8° (*c* 0.6, MeOH); ^{1}H NMR (C_5D_5N) 5.72 (1H, d, *J* = 5.1 Hz, H-6), 4.83 (1H, t, *J* = 6.4 Hz, H-16), 4.79 (2H, br s, H_2-27), 4.46 (1H, d, *J* = 11.9, H-26), 3.97 (1H, d, *J* = 11.9, H-26), 3.93 (1H, m, H-3), 3.88 (1H, dd, *J* = 11.7, 4.1 Hz, H-1), 2.43 (1H, q, *J* = 7.3 Hz, H-20), 2.34 (1H, dt, *J* = 11.9, 4.6 Hz, H-9), 2.17 (1H, dt, *J* = 11.5, 4.6 Hz, H-8), 1.44 (3H, s, H_3-19), 1.21 (3H, s, H_3-18), 1.20 (3H, d, *J* = 7.3 Hz, H_3-21); ^{13}C NMR, see Table 1; FABMS *m/z* 459.3 [M-H]$^-$; HRFABMS *m/z* 459.2751 (calcd for [M-H]$^-$ 459.2746).

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