Two New Steroidal Saponins from Dried Fermented Residues of Leaf-Juices of *Agave sisalana* forma Dong No. 1

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In a previous paper, we reported the isolation and structure determination of three new steroidal saponins, dongnosides C (3), D (2) and E (1) from the dried fermented residues of leaf-juices of *Agave sisalana* forma Dong No. 1. In a continuing study on this plant, two additional new major steroidal saponins, named dongnosides B (4) and A (5), were obtained. Their structures were characterized respectively as tigogenin 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- β -D-glucopyranosyl-(1 $\rightarrow$ 2)-[β -D-glucopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranosyl-(1 $\rightarrow$ 4)- β -D-galactopyranoside and 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)- β -D-glucopyranosyl-(1 $\rightarrow$ 2)-[β -D-xylopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranosyl-(1 $\rightarrow$ 4)- β -D-galactopyranoside on the basis of chemical and physicochemical evidence.

Keywords *Agave sisalana*; Agavaceae; steroidal saponin; spirostanol glycoside; tigogenin; dongnoside

Agave sisalana PERRINE is a plant of *Agave* Linne genus, Agavaceae family. It was introduced from abroad and has been cultivated in the south of China, named "Agave Dong No. 1." Its leaves are a very important source of hard fiber and raw material used to synthesize steroidal hormones. In a previous paper, we have reported the isolation and structure elucidation of three new steroidal saponins, dongnoside C (3), D (2) and E (1) from *Agave* Dong No. 1.¹⁾ As a further study, we have isolated two more new steroidal saponins, named dongnosides B (4) and A (5), and have characterized their structures.

The dried fermented residues²⁾ (3.0 kg) of leaf-juices of *Agave* Dong No. 1 were refluxed with petroleum ether (petrol, 60–80°C), and the petrol-insoluble residue was extracted with methanol (MeOH). The MeOH extract was evaporated under reduced pressure to give a residue (774 g) which was separated by column chromatography (CC) and preparative thin layer chromatography (TLC) over silica gel (Si gel), to provide compounds 1 (110 mg), 2 (1.25 g), 3 (186 mg), 4 (1.30 g) and 5 (3.60 g).

The saponins B (4) and A (5) were positive in the Liebermann–Burchard reaction, but negative to the Ehrlich reagent.³⁾ They showed the characteristic absorption band⁴⁾ of 25*R* spirostanol steroid [985, 920<900 (in intensity), 870 cm⁻¹] and hydroxyl group absorptions (3440–3460 and 1050–1080 cm⁻¹) in the infrared (IR) spectrum, suggesting that saponins 4 and 5 are the glycosides of the 25*R* spirostanol derivative.

Dongnoside B (4), a white powder (mp 275–277°C), [α]_D –50.8° (pyridine), showed peaks due to a [M–H][–] ion at *m/z* 1209 in the negative fast atom bombardment mass spectrum (negative FAB-MS), and the elementary analysis of 4 indicated the molecular formula C₅₇H₉₄O₂₇. Acid hydrolysis of 4 afforded rhamnose, galactose and glucose as the sugar components, and an aglycone, colorless needles (MeOH), mp 206–208°C, [α]_D –51.7° (pyridine). The electron impact mass spectrum (EI-MS) showed a molecular ion peak at *m/z* 416 and a characteristic base peak at *m/z* 139 (C₉H₁₅O) derived from the spiroketal side chain of the steroidal sapogenol.⁵⁾ The molecular formula C₂₇H₄₄O₃ was determined by elementary analysis and EI-MS. Comparison of carbon-13 nuclear magnetic res-

onance (¹³C-NMR) data for the aglycone (Table I) with those of tigogenin,⁶⁾ indicated aglycone was tigogenin, (5 α ,25*R*)-3 β -hydroxy-spirostanane. In the negative FAB-MS spectrum, in addition to a molecular ion peak, fragment ion peaks at *m/z* 1063 and 901 were found, which were ascribable to fragments due to the loss of terminal rhamnose and rhamnopyranosyl-hexosyl residues, respectively. Saponin 4 was acetylated in the usual manner to yield a peracetate, [α]_D –27.0° (MeOH), showing fragment peaks at *m/z* 561 [(Rha–Hex–)Ac₆]⁺, 331 [(terminal Hex–)Ac₄]⁺ and 273 [(terminal Rha–)Ac₃]⁺ in the EI-MS. The above evidence suggested that 4 was a tigogenin pentaglycoside consisting of 4 mol of hexose and 1 mol of rhamnose in which 1 mol

TABLE I. ¹³C-NMR Chemical Shifts for Aglycone Moieties of Saponins 4, 5 and Prosapogenins 4b, 4c, 4d, 5e and Tigogenin (Pyridine-*d*₅)

	Tigogenin	4b	4c	4	4d	5	5e
C -1	37.5	37.1	37.1	37.2	37.1	37.2	37.2
C -2	32.5	30.5	30.6	29.9	30.5	30.6	29.9
C -3	70.6	77.1	77.5	77.4	77.5	77.4	77.4
C -4	39.3	34.7	34.8	34.8	34.7	34.8	34.8
C -5	45.2	44.8	44.8	44.6	44.6	44.6	44.6
C -6	29.1	28.8	28.9	28.9	28.9	28.9	28.9
C -7	32.5	32.3	32.4	32.4	32.4	32.2	32.4
C -8	35.4	35.2	35.3	35.2	35.3	35.2	35.2
C -9	54.6	54.3	54.5	54.4	54.3	54.4	54.4
C-10	35.9	35.7	35.8	35.8	35.8	35.8	35.8
C-11	21.1	21.2	21.3	21.3	21.2	21.3	21.3
C-12	40.3	40.0	40.2	40.1	40.1	40.1	40.1
C-13	40.8	40.7	40.8	40.7	40.7	40.8	40.8
C-14	57.6	56.4	56.5	56.4	56.4	56.4	56.4
C-15	32.1	32.1	32.1	32.1	32.1	32.1	32.2
C-16	81.1	81.1	81.1	81.1	81.1	81.1	81.1
C-17	63.1	63.0	63.0	63.0	62.9	63.0	63.0
C-18	16.7	16.6	16.6	16.6	16.6	16.6	16.6
C-19	12.5	12.2	12.3	12.3	12.3	12.3	12.3
C-20	42.0	41.9	42.0	42.0	41.9	42.0	42.0
C-21	15.0	14.9	15.0	15.0	15.0	15.0	15.0
C-22	109.2	109.1	109.2	109.2	109.2	109.2	109.2
C-23	31.9	31.7	31.8	31.8	31.8	31.8	31.8
C-24	29.3	29.2	29.2	29.2	29.2	29.2	29.2
C-25	30.6	29.9	29.9	30.0	29.8	30.0	30.6
C-26	66.9	66.9	66.9	66.9	66.8	66.9	66.8
C-27	17.3	17.3	17.3	17.3	17.3	17.3	17.3

TABLE II. ^{13}C -NMR Chemical Shifts for Sugar Moieties of Saponins **4**, **5** and Prosapogenins **4b**, **4c**, **4d**, and **5e** (Pyridine- d_5)

	4b	4c	4d	4	5e	5
Gal						
1	102.4	102.3	102.3	102.4	102.4	102.4
2	73.4	73.2	73.1	73.1	73.1	73.1
3	75.2	75.0	75.2	75.2	75.0	75.0
4	80.0	78.9	81.3	81.4	80.8	80.8
5	76.0	76.7	76.0	76.6	75.4	76.5
6	61.0	60.4	60.6	60.6	60.6	60.6
Glc						
1	107.1	105.1	104.3	104.1	104.0	103.9
2	75.4	75.5	80.1	80.1	79.9	79.8
3	78.4	86.0	88.1	87.9	88.4	88.0
4	72.2	70.2	70.7	70.6	69.0	70.6
5	78.7	78.1	77.4	77.3	78.6	78.0
6	63.0	61.5	62.3	62.2	62.3	62.0
Glc'						
1			104.7	104.7	104.8	104.7
2			75.4	75.3	75.3	75.5
3			78.5	77.1	78.4	77.2
4			71.5	78.5	71.6	78.1
5			77.4	76.0	78.1	75.5
6			62.1	61.1	63.0	61.1
Glc''						
1		106.8	104.5	104.9	104.4	104.1
2		75.6	75.2	75.5	75.3	75.3
3		78.9	78.5	78.4	86.8	86.9
4		71.7	70.8	70.9	70.7	70.7
5		78.4	77.3	77.9	77.5	77.4
6		62.9	62.9	62.9	62.0	62.9
Xyl						
1					106.0	106.1
2					75.4	75.3
3					77.7	77.4
4					70.7	70.3
5					67.0	67.0
Rha						
1				102.6		102.6
2				72.4		72.5
3				72.6		72.7
4				73.8		73.9
5				70.4		69.1
6				18.5		18.5

each of rhamnose and hexose was located at the terminal. The ^1H -NMR spectrum of **4** exhibited five anomeric proton signals, among which four doublet signals at δ 4.87 ($J=7.3$ Hz), 5.11 ($J=7.7$ Hz), 5.27 ($J=7.7$ Hz) and 5.56 ($J=7.7$ Hz) suggested all β -configurations of glucosyl and galactosyl moieties, while one singlet signal at δ 5.73 was attributable to the α -one of the rhamnosyl moiety. Partial hydrolysis of **4** with 0.5N HCl in 50% EtOH provided four prosapogenins, **4a**, **4b**, **4c** and **4d**. The former three were the same as the hydrolyzed products of **1**,¹⁾ identified with 3-*O*-monoglycoside, 3-*O*-diglycoside and 3-*O*-triglycoside of tigogenin, respectively. Compound **4d** showed the presence of four anomeric carbons at δ 102.3, 104.3, 104.5 and 104.7 in the ^{13}C -NMR spectrum (Table II), and the peracetate of **4d** gave a fragment peak at m/z 331. On acid hydrolysis, **4d** liberated glucose and galactose. The above evidence indicated that **4d** is a 3-*O*-tetraglycoside with a terminal hexose. In comparing of the ^{13}C -NMR spectrum (Table II) of **4d** with **4c**, **4d** showed signals due to one additional mole of glucose compared to **4c**, as well as a downfield shift (+4.6 ppm) at C-2 of the inner glucose, indicating that **4d** should possess 1 mol more of glucose

Fig. 1. ^1H - ^1H COSY and NOESY of 5-M-1

than **4c** and that the terminal glucose branched at C-2 OH of the inner glucose. Thus, **4d** was characterized as tigogenin 3-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)-[β -D-glucopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranosyl-(1 $\rightarrow$ 4)- β -D-galactopyranoside. The ^{13}C -NMR spectrum (Table II) of **4** showed increased signals due to the terminal rhamnose compared to those of **4d**, and displayed that the signal due to C-4 of one glucose shifted by +7.0 ppm, suggesting that a rhamnose was attached to the C-4 OH of one glucose in **4**. The question of whether the terminal rhamnosyl residue combines to C-2 or C-3 glucose remains unsolved in this stage; however, this could be settled after determining for the structure of the following compound, dongnoside A (**5**).

Dongnoside A (**5**), white powder, (mp 265–270 $^{\circ}\text{C}$), $[\alpha]_{\text{D}} -51.5^{\circ}$ (pyridine), gave the molecular formula $\text{C}_{62}\text{H}_{102}\text{O}_{31}$ by elementary analysis. Acid hydrolysis of **5** with 2N H_2SO_4 in 50% EtOH yielded tigogenin, glucose, galactose, xylose and rhamnose. The negative FAB-MS of **5** showed a molecular ion peak at m/z 1341 $[\text{M}-\text{H}]^{-}$ and fragment peaks due to $[\text{M}-\text{H}-\text{Pen}]^{-}$ at m/z 1209, $[\text{M}-\text{H}-\text{Rha}]^{-}$ at m/z 1195, $[\text{M}-\text{H}-\text{Pen}-\text{Hex}]^{-}$ at m/z 1047 and $[\text{M}-\text{H}-\text{Rha}-\text{Hex}]^{-}$ at m/z 1033. The EI-MS of **5**-peracetate gave fragment peaks at m/z 273 [(terminal Rha-)Ac $_3$] $^{+}$ and 259 [(terminal Pen-)Ac $_3$] $^{+}$, suggesting that **5** was composed of 4 mol of hexose and 1 mol each of rhamnose and xylose, and in addition, that the rhamnose and xylose were located at the terminal. In the ^1H -NMR spectrum, **5** exhibited five doublet signals at δ 4.84 ($J=7.6$ Hz), 5.06 ($J=7.3$ Hz), 5.08 ($J=7.3$ Hz), 5.16 ($J=7.6$ Hz) and 5.53 ($J=7.3$ Hz) assigned to the anomeric protons of glucose, galactose and xylose, and a singlet signal at δ 5.76 assignable to rhamnose, suggesting that rhamnose is α -linked and the other sugar moieties are β -linked. On partial hydrolysis, **5** afforded two main prosapogenins identical with **4** and **4d**. The ^{13}C -NMR spectrum (Table II) of **5** compared with that of **4** indicated an increase in signals due to 1 mol of xylose in **5** and its glycosylation shift (+8.4 ppm) at C-3 of the inner glucose. On the other hand, enzymatic hydrolysis of **5** with hesperidinase provided rhamnose and a prosapogenin, **5e**. A comparative study of the ^{13}C -NMR spectrum of **5** and **5e** suggested that signals due to a terminal rhamnose increased with a glycosylation

C-M-W (7:3:1 lower phase) and 1 ml of AcOH.

Acetylation of 4 A solution of **4** (30 mg) in 3 ml Ac₂O-pyridine (2:1) was kept at room temperature for 2 d. The reaction mixture was poured into ice water and the precipitate was collected by filtration to afford the peracetate, **4-A**, a white powder, $[\alpha]_D^{25} -27.0^\circ$ ($c=0.06$, MeOH). IR $\nu_{\max}^{\text{film}}$ cm⁻¹: no OH, 1750 (C=O), 1225 (C-O), 980, 920 < 900, 840 (25R spirostanol). EI-MS m/z : 561 [(Rha-Hex-Ac)₆]⁺, 331 [(terminal Hex-Ac)₄]⁺, 273 [(terminal Rha-Ac)₃]⁺.

Partial Acid Hydrolysis of 4 Compound **4** (1 g) was suspended in 0.5 N HCl-50% EtOH and was heated at 85°C for 20 min. Partition of the reaction mixture was attained between CHCl₃ and water, followed by water-saturated 1-BuOH and water. The CHCl₃ layer and 1-BuOH layer were combined, evaporated *in vacuo*, and chromatographed on Si gel with C-M-W (7:3:1 lower phase) to afford **4a** (10.5 mg), **4b** (17.2 mg), **4c** (20.1 mg) and **4d** (154 mg). Compounds **4a**, **4b** and **4c** were identified with **1a**, **1b** and **1c**, respectively by ¹³C-NMR. **4d**, ¹³C-NMR (pyridine-*d*₅): Tables I and II. **4d-A** (peracetate), EI-MS m/z : 331 [(terminal Hex-Ac)₄]⁺.

Dongnoside A (5) A white powder (mp 265–270°C), $[\alpha]_D^{25} -51.5^\circ$ ($c=0.07$, pyridine). IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3450–3470, 1060–1080 (–OH), 985, 920 < 900, 865, 815 (25R spirostanol). ¹H-NMR (pyridine-*d*₅) δ : 0.65 (3H, s, CH₃-18), 0.71 (3H, d, $J=5.1$ Hz, CH₃-27), 0.83 (3H, s, CH₃-19), 1.16 (3H, d, $J=7.0$ Hz, CH₃-21), 1.68 (3H, d, $J=5.9$ Hz, Rha CH₃), 3.51–3.62 (2H, m, H₂-26), 4.84 (1H, d, $J=7.6$ Hz), 5.06 (1H, d, $J=7.3$ Hz), 5.08 (1H, d, $J=7.3$ Hz), 5.16 (1H, d, $J=7.6$ Hz), 5.53 (1H, d, $J=7.3$ Hz), 5.76 (1H, br s). Negative FAB-MS m/z : 1341 [M-H][–], 1209 [M-H-Pen][–], 1195 [M-H-Rha][–], 1047 [M-H-Hex-Pen][–], 1033 [M-H-Hex-Rha][–], 901 [M-H-Hex-Pen-Rha][–], 739 [M-H-2×Hex-Pen-Rha][–], 577 [M-H-3×Hex-Pen-Rha][–], 413 [M-3H-4×Hex-Pen-Rha][–]. Anal. Calcd for C₆₂H₁₀₂O₃₁·2H₂O: C, 53.99; H, 7.69. Found: C, 53.96; H, 7.56. ¹³C-NMR (pyridine-*d*₅): Tables I and II.

Acetylation of 5 A solution of compound **5** (30 mg) was acetylated in the same manner as **4** to afford the peracetate (**5-A**), a white powder, $[\alpha]_D^{25} -26.7^\circ$ ($c=0.09$, MeOH). IR $\nu_{\max}^{\text{film}}$ cm⁻¹: no OH, 1750 (C=O), 1225 (C-O), 980, 920 < 900, 840 (25R spirostanol). EI-MS m/z : 561 [(Rha-Hex-Ac)₆]⁺, 547 [(Pen-Hex-Ac)₆]⁺, 273 [(terminal Rha-Ac)₃]⁺, 259 [(terminal Pen-Ac)₃]⁺.

Enzymic Hydrolysis of 5 A mixture of compound **5** (128.6 mg) and hesperidinase (50 mg) (from Penicillium species, Sigma Chemical Co.) in citrate buffer (pH 5.0, 4 ml) and dimethyl sulfoxide (DMSO, 1 ml) was incubated at 37°C for 3 d. The reaction mixture was evaporated to dryness and dissolved in CHCl₃ and MeOH. The filtrate was chromatographed over Si gel with C-M-W (7:3:0.2) to afford **5e** (53.3 mg). ¹H-NMR (pyridine-*d*₅) δ : 0.64 (3H, s, CH₃-18), 0.70 (3H, d, $J=5.1$ Hz, CH₃-27), 0.83 (3H, s, CH₃-19), 1.14 (3H, d, $J=7.0$ Hz, CH₃-21), 3.49–3.61 (2H, m, H₂-26), 4.88 (1H, d, $J=7.7$ Hz), 5.10 (1H, d, $J=7.3$ Hz), 5.14 (1H, d, $J=7.7$ Hz), 5.21 (1H, d, $J=7.7$ Hz), 5.57 (1H, d, $J=7.3$ Hz). ¹³C-NMR (pyridine-*d*₅): Tables I and II. **5e-A** (peracetate of **5e**), EI-MS m/z : 331 [(terminal Hex-Ac)₄]⁺, 259 [(terminal Pen-Ac)₃]⁺.

Permethylolation of 5, Subsequent Partial Hydrolysis and Acetylation A solution of glycoside **5** (142 mg) in DMSO (3 ml) was added to the preheated (70°C, 30 min) mixture of DMSO (3 ml) and NaH (200 mg) and was kept at 70°C for another 20 min. Then CH₃I (4 ml) was added and kept at room temperature for 3 h. To the reaction mixture, water and CHCl₃ were added and shaken. The organic layer was concentrated to give a resinous liquid, to which ether and water were added. The organic layer was evaporated under reduced pressure to afford a residue, which was purified by Si gel CC with *n*-hexane-acetone (Hex-Ace, 4:1) as a solvent to provide a permethyl ether (**5-M**, 56 mg). IR no OH. ¹H-NMR (CDCl₃) δ : 0.76 (3H, s, CH₃-18), 0.79 (3H, d, $J=6.2$ Hz, CH₃-27), 0.82 (3H, s, CH₃-19), 0.96 (3H, d, $J=7.0$ Hz, CH₃-21), 3.35, 3.37, 3.40, 3.42, 3.44, 3.46, 3.47, 3.50, 3.52 (×2), 3.55, 3.56 (×2), 3.57, 3.59 (×2), 3.61 (16×CH₃), 4.30 (1H, d, $J=7.7$ Hz, Gal H-1), 4.39 (1H, ddd, $J=7.4, 7.4, 7.4$ Hz, H-16), 4.73 (1H, d, $J=7.3$ Hz, Glc H-1), 4.79 (1H, d, $J=7.3$ Hz, Glc' H-1), 4.81 (1H, d, $J=7.7$ Hz, Glc' H-1), 4.99 (1H, d, $J=7.7$ Hz, Xyl H-1), 5.02 (1H, s, Rha H-1).

The permethyl ether (**5-M**, 49.4 mg) was partially hydrolyzed with 0.5 N

HCl-MeOH (1.5 ml) for 60 min on the water bath. The usual work-up of the reaction mixture and separation by Si gel CC using Hex-Ace (4:1) as an eluting solvent afforded three main compounds, which were subsequently acetylated with Ac₂O and pyridine to yield the corresponding acetates, **5-M-1** (14.5 mg), **5-M-2** (6.5 mg) and **5-M-3** (5.2 mg).

5-M-1: A white powder, positive FAB-MS m/z : 1326 [M+Na+H]⁺, 1302 [M]⁺. ¹H-NMR (CDCl₃) δ : 0.76 (3H, s, CH₃-18), 0.79 (3H, d, $J=6.6$ Hz, CH₃-27), 0.81 (3H, s, CH₃-19), 0.96 (3H, d, $J=7.0$ Hz, CH₃-21), 2.09, 2.11 (each 3H, s, 2×OAc), 4.38 (1H, ddd, $J=7.5, 7.5, 7.5$ Hz, H-16), 4.31 (1H, d, $J=7.3$ Hz, Gal H-1), 3.56 (1H, m, Gal H-2), 3.08 (1H, dd, $J=3.1, 10.1$ Hz, Gal H-3), 4.08 (1H, d, $J=3.1$, Gal H-4), 4.74 (1H, d, $J=7.3$ Hz, Glc H-1), 3.75 (1H, t, $J=7.7$ Hz, Glc H-2), 4.05 (1H, t, $J=8.4$ Hz, Glc H-3), 3.21 (1H, t, $J=9.3$ Hz, Glc H-4), 5.13 (1H, d, $J=7.9$ Hz, Glc' H-1), 3.02 (1H, t, $J=8.4$ Hz, Glc' H-2), 3.31 (1H, t, $J=9.3$ Hz, Glc' H-3), 4.81 (1H, t, $J=9.5$ Hz, Glc' H-4), 4.92 (1H, d, $J=7.7$ Hz, Glc' H-1), 3.01 (1H, t, $J=8.1$ Hz, Glc'' H-2), 5.12 (1H, t, $J=9.0$ Hz, Glc'' H-3), 3.15 (1H, t, $J=9.1$ Hz, Glc'' H-4).

5-M-2: A white powder, positive FAB-MS m/z : 1458 [M+Na+H]⁺. ¹H-NMR (CDCl₃) δ : 0.76 (3H, s, CH₃-18), 0.79 (3H, d, $J=6.2$ Hz, CH₃-27), 0.82 (3H, s, CH₃-19), 0.96 (3H, d, $J=6.6$ Hz, CH₃-21), 2.11 (3H, s, OAc), 4.39 (1H, ddd, $J=7.7, 7.7, 7.7$ Hz, H-16), 4.31 (1H, d, $J=7.7$ Hz, Gal H-1), 3.53 (1H, m, Gal H-2), 3.08 (1H, dd, $J=3.7, 9.2$ Hz, Gal H-3), 4.06 (1H, d, $J=3.1$, Gal H-4), 4.73 (1H, d, $J=7.3$ Hz, Glc H-1), 3.73 (1H, t, $J=8.1$ Hz, Glc H-2), 4.04 (1H, t, $J=8.4$ Hz, Glc H-3), 3.25 (1H, t, $J=9.3$ Hz, Glc H-4), 4.92 (1H, d, $J=7.7$ Hz, Glc' H-1), 3.01 (1H, t, $J=9.2$ Hz, Glc' H-2), 3.25 (1H, t, $J=9.3$ Hz, Glc' H-3), 4.83 (1H, t, $J=9.5$ Hz, Glc' H-4), 4.75 (1H, d, $J=7.3$ Hz, Glc'' H-1), 2.94 (1H, t, $J=8.1$ Hz, Glc'' H-2), 3.14 (1H, t, $J=8.1$ Hz, Glc'' H-3), 3.25 (1H, t, $J=9.3$ Hz, Glc'' H-4), 5.01 (1H, d, $J=7.7$ Hz, Xyl H-1), 3.08 (1H, t, $J=9.3$ Hz, Xyl H-2), 3.78 (1H, t, $J=9.2$ Hz, Xyl H-3), 3.05 (1H, m, Xyl H-4).

5-M-3: A white powder, positive FAB-MS m/z : 1472 [M+Na+H]⁺. ¹H-NMR (CDCl₃) δ : 0.76 (3H, s, CH₃-18), 0.79 (3H, d, $J=6.2$ Hz, CH₃-27), 0.81 (3H, s, CH₃-19), 0.96 (3H, d, $J=7.0$ Hz, CH₃-21), 1.29 (3H, d, $J=6.2$ Hz, Rha CH₃), 4.31 (1H, d, $J=7.7$ Hz, Gal H-1), 4.79 (1H, d, $J=7.0$ Hz, Glc H-1), 3.77 (1H, t, $J=7.3$ Hz, Glc H-2), 4.01 (1H, t, $J=8.4$ Hz, Glc H-3), 3.20 (1H, t, $J=9.2$ Hz, Glc H-4), 5.10 (1H, d, $J=7.8$ Hz, Glc' H-1), 4.81 (1H, d, $J=7.0$ Hz, Glc'' H-1), 3.04 (1H, t, $J=8.1$ Hz, Glc'' H-2), 5.11 (1H, t, $J=9.2$ Hz, Glc'' H-3), 3.21 (1H, t, $J=9.3$ Hz, Glc'' H-4), 5.01 (1H, br s, Rha H-1).

Acknowledgements The authors are grateful to the Analytical Laboratory of the Institute of Materia Medica, Chinese Academy of Medical Science, Kunming Institute of Botany, Academia Sinica and Mr. K. Takeda and Mr. T. Iriguchi of Kumamoto University for elemental analysis, $[\alpha]_D$, IR, NMR, EI-MS. We are also grateful to Dr. M. L. Chang (Columbia University, U.S.A.) for measurement of FAB-MS.

References and Notes

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