

**MEDICINAL FOODSTUFFS. VIII.<sup>1</sup> FENUGREEK SEED. (2) :  
STRUCTURES OF SIX NEW FUROSTANOL SAPONINS,  
TRIGONEOSIDES IVa, Va, Vb, VI, VIIb, AND VIIIb, FROM  
THE SEEDS OF INDIAN *TRIGONELLA FOENUM-GRÆCUM* L.<sup>†</sup>**

Masayuki Yoshikawa,\* Toshiyuki Murakami, Hajime Komatsu, Johji Yamahara, and  
Hisashi Matsuda

Kyoto Pharmaceutical University, 5 Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607,  
Japan

**Abstract** — Following the characterization of trigoneosides Ia, Ib, IIa, IIb, IIIa, and IIIb, seven new steroidal saponins called trigoneosides IVa, Va, Vb, VI, VIIb, VIIIb, and IX were isolated from a medicinal foodstuff fenugreek seed, the seeds of *Trigonella foenum-græcum* L. (Leguminosae) originating from India. The structures of trigoneosides IVa, Va, Vb, VI, VIIb, and VIIIb were elucidated on the basis of chemical and physicochemical evidence.

In the previous paper,<sup>2</sup> we reported the isolation of six furostanol saponins, trigoneosides Ia, Ib, IIa, IIb, IIIa, and IIIb, from a medicinal foodstuff fenugreek seed ("Koroha" in Japanese), the seeds of *Trigonella foenum-græcum* L. (Leguminosae) originating from India and their structure elucidations. In a continuing study, we have isolated seven new furostanol saponins called trigoneosides IVa (1), Va (2), Vb (3), VI (4), VIIb (5), VIIIb (6), and IX from the polar fraction of the glycoside fraction from Indian fenugreek seed together with three known furostanol saponins, compound C (7),<sup>3</sup> glycoside F (8),<sup>4</sup> and trigonelloside C (9).<sup>5</sup> This paper offers the isolation of the polar saponins and the structure elucidations of trigoneosides IVa (1), Va (2), Vb (3), VI (4), VIIb (5), and VIIIb (6) on the basis of chemical and physicochemical evidence.<sup>6</sup>

**Trigoneoside IVa (1)**

Trigoneoside IVa (1) was isolated as a white powder and was deduced to possess a furostanol structure by TLC examination using the Ehrlich reagent.<sup>7</sup> The IR spectrum of 1 showed strong absorption bands at 3410, 1072, and 1052 cm<sup>-1</sup> suggestive of oligoglycosidic structure. The negative-ion and positive-ion FABMS of 1 showed quasimolecular ions at *m/z* 1063 (M-H)<sup>-</sup> and *m/z* 1087 (M+Na)<sup>+</sup>, respectively, and high-resolution MS analysis revealed the molecular formula of 1 to be C<sub>51</sub>H<sub>84</sub>O<sub>23</sub>. Methanolysis of 1 with 9% hydrogen chloride in dry methanol liberated yamogenin (10)<sup>5b,8</sup> having the 25*S*-configuration as the sapogenol and the methyl glycosides of glucose and rhamnose in a ca. 3 : 1 ratio.<sup>9</sup> The <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) and <sup>13</sup>C-NMR (Table 1) spectra of 1, which were assigned by various NMR analytical methods,<sup>10</sup> indicated the presence of the furost-5-ene moiety [δ 0.90 (s, 18-H<sub>3</sub>), 1.03 (d, *J*=6.7 Hz, 27-H<sub>3</sub>), 1.06 (s, 19-H<sub>3</sub>), 1.33 (d, *J*=7.1 Hz, 21-H<sub>3</sub>), 2.24 (dq, *J*=6.9, 6.9 Hz, 20-H), 5.29 (d-like, 6-H)], 3-*O*-β-D-glucopyranosyl part [δ 4.95 (d, *J*=9.0 Hz, 1'-H)], 2'-*O*-α-L-rhamnopyranosyl part [δ 1.77 (d, *J*=6.4 Hz, 6"-H<sub>3</sub>), 6.26 (br s, 1"-H)], 4'-*O*-β-D-glucopyranosyl part [δ 5.14 (d, *J*=8.0 Hz, 1'''-H)], and 26-*O*-β-D-

<sup>†</sup> Dedicated to Dr. Koji Nakanishi, Professor Columbia University, in the celebration of his 75th birthday.

glucopyranosyl part [ $\delta$  4.82 (d,  $J=8.0$  Hz, 1<sup>'''</sup>-H)]. The proton and carbon signals in the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of **1** were shown to be superimposable on those of glycoside **F** (**8**), except for the proton signals due to the 26-methylene group [ $\delta$  3.49 (dd,  $J=7.1, 9.5$  Hz), 4.09 (dd,  $J=6.1, 9.5$  Hz)], which were very similar to those of 26-*O*- $\beta$ -D-glucopyranosyl-25(*S*)-furostanol glycosides such as trigoneosides **Ia**, **Ila**, and **IIla**.<sup>2</sup> The 3,26-bisdesmoside structure of **1** was clarified by a heteronuclear multiple bond correlation (HMBC) experiment. Thus, long-range correlations were observed between the 1<sup>'''</sup>-proton and the 4'-carbon, between the 1<sup>''</sup>-proton and the 2'-carbon, between the 1'-proton and 3-carbon, and between the 1<sup>'''</sup>-proton and the 26-carbon. Consequently, the structure of trigoneoside **IVa** was determined to be as 26-*O*- $\beta$ -D-glucopyranosyl-(25*S*)-furost-5-ene-3 $\beta$ ,22 $\xi$ ,26-triol 3-*O*-[ $\alpha$ -L-rhamnopyranosyl (1 $\rightarrow$ 2)] [ $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 4)]- $\beta$ -D-glucopyranoside (**1**).

#### Trigoneosides **Va** (**2**) and **Vb** (**3**)

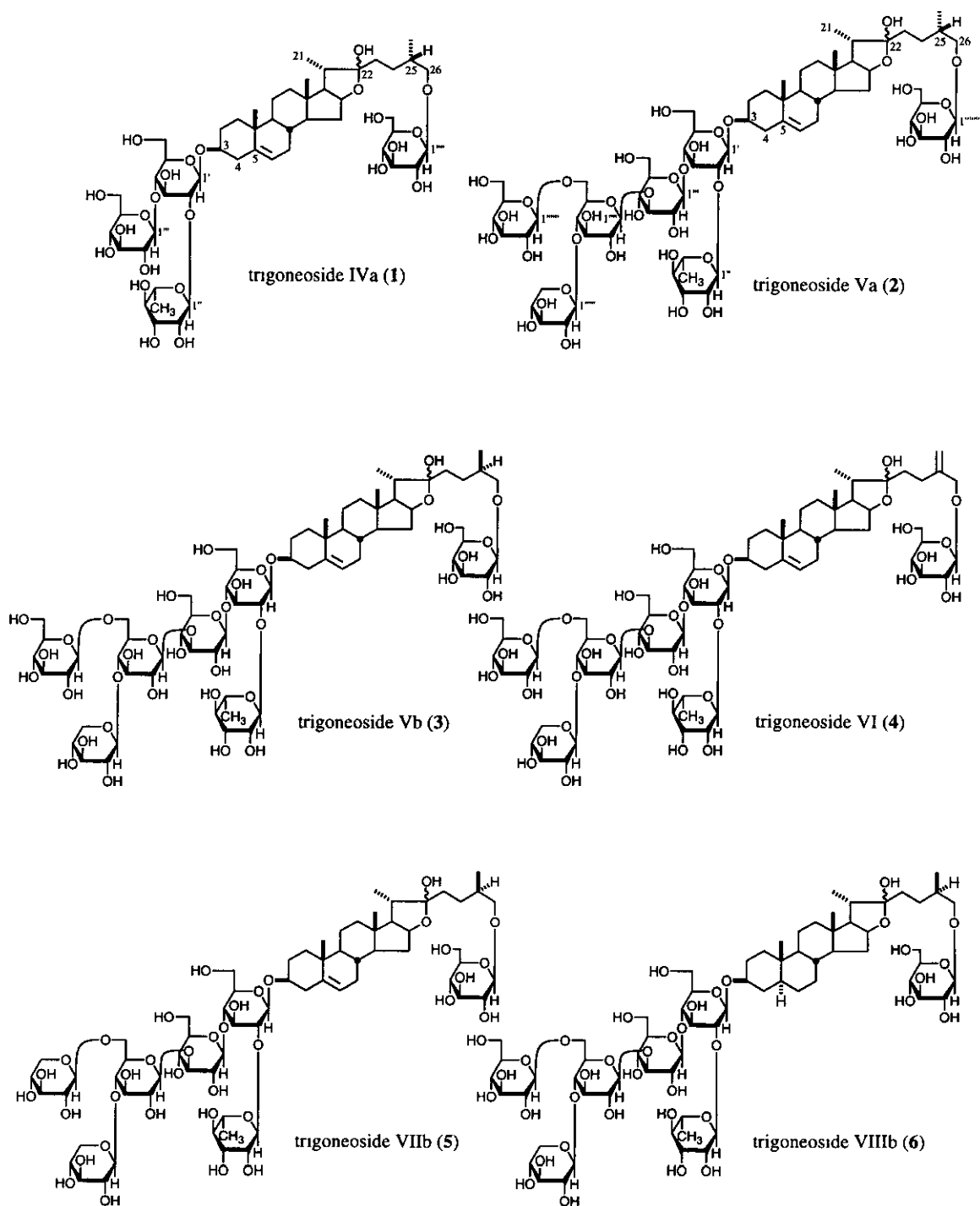
Trigoneosides **Va** (**2**) and **Vb** (**3**) were also isolated as a white powder and were deduced to possess a furostanol structure based on the positive Ehrlich test. The IR spectra of **2** and **3** showed strong absorption bands due to the oligoglycoside structure. Trigoneosides **Va** (**2**) and **Vb** (**3**) were found to have the same molecular formula C<sub>68</sub>H<sub>112</sub>O<sub>37</sub>, which was determined from their negative-ion and positive-ion FABMS and by high-resolution MS measurement. Thus, in the negative-ion FABMS of **2** and **3**, the quasimolecular ion peak was observed at  $m/z$  1519 (M-H)<sup>-</sup>, while their positive-ion FABMS showed the quasimolecular ion peak at  $m/z$  1543 (M+Na)<sup>+</sup>. Furthermore, fragment ion peaks were observed at  $m/z$  1387 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>,  $m/z$  1357 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>,  $m/z$  1063 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>, and  $m/z$  901 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup> in the negative-ion FABMS of **2** and **3**. Methanolysis of **2** and **3** liberated yamogenin (**10**) and diosgenin (**11**)<sup>5b,8</sup> as the sapogenol, respectively, together with their common methyl glycosides of glucose, rhamnose, and xylose in a *ca.* 5 : 1 : 1 ratio.<sup>9</sup> Acid hydrolysis of **3** with 5% aqueous sulfuric acid-1,4-dioxane (1 : 1, v/v) furnished D-glucose, L-rhamnose, and D-xylose, which were identified by GLC analysis of their trimethylsilyl thiazolidine derivatives.<sup>11</sup>

The <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) and <sup>13</sup>C-NMR (Table 1) spectra<sup>10</sup> of **2** showed signals ascribable to the 25*S*-furost-5-ene part [ $\delta$  0.90 (s, 18-H<sub>3</sub>), 1.04 (d,  $J=6.7$  Hz, 27-H<sub>3</sub>), 1.07 (s, 19-H<sub>3</sub>), 1.33 (d,  $J=6.7$  Hz, 21-H<sub>3</sub>), 2.24 (dq,  $J=7.0, 7.0$  Hz, 20-H), 3.50 (dd,  $J=7.1, 9.2$  Hz), 4.09 (m, 26-H<sub>2</sub>), 5.29 (br s, 6-H)], five  $\beta$ -D-glucopyranosyl moieties [ $\delta$  4.83 (d,  $J=7.7$  Hz, 1<sup>''''</sup>-H), 4.95 (d-like, 1'-H), 5.08 (d-like, 1<sup>'''</sup>-H), 5.24 (d,  $J=8.0$  Hz, 1<sup>'''</sup>-H), 5.28 (d,  $J=8.0$  Hz, 1<sup>''''</sup>-H)],  $\alpha$ -L-rhamnopyranosyl moiety [ $\delta$  1.78 (d,  $J=6.1$  Hz, 6''-H<sub>3</sub>), 6.25 (br s, 1''-H)], and  $\beta$ -D-xylopyranosyl moiety [ $\delta$  5.33 (d,  $J=7.6$  Hz, 1<sup>''''</sup>-H)]. The carbon signals of the 26-*O*- $\beta$ -D-glucopyranosyl-(25*S*)-furost-5-ene-3 $\beta$ ,22 $\xi$ ,26-triol moiety in the <sup>13</sup>C-NMR spectrum of **2** were found to be superimposable on those of trigoneoside **IVa** (**1**) and compound **C** (**7**). The HMBC experiment of **2** showed long-range correlations between the following protons and carbons : 1<sup>''''</sup>-H and 6<sup>'''</sup>-C, 1<sup>'''</sup>-H and 4<sup>'''</sup>-C, 1<sup>''</sup>-H and 3<sup>'''</sup>-C, 1<sup>'</sup>-H and 4'-C, 1<sup>'</sup>-H and 2'-C, 1'-H and 3-C, 1<sup>''''</sup>-H and 26-C, so that the 3,26-bisdesmoside structure of **2** was characterized. On the basis of this evidence, the structure of trigoneoside **Va** was formulated as 26-*O*- $\beta$ -D-glucopyranosyl-(25*S*)-furost-5-ene-3 $\beta$ ,22 $\xi$ ,26-triol 3-*O*-[ $\alpha$ -L-rhamnopyranosyl (1 $\rightarrow$ 2)] {[ $\beta$ -D-xylopyranosyl (1 $\rightarrow$ 4)] [ $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 6)]- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 3)]- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 4)]- $\beta$ -D-glucopyranoside (**2**).

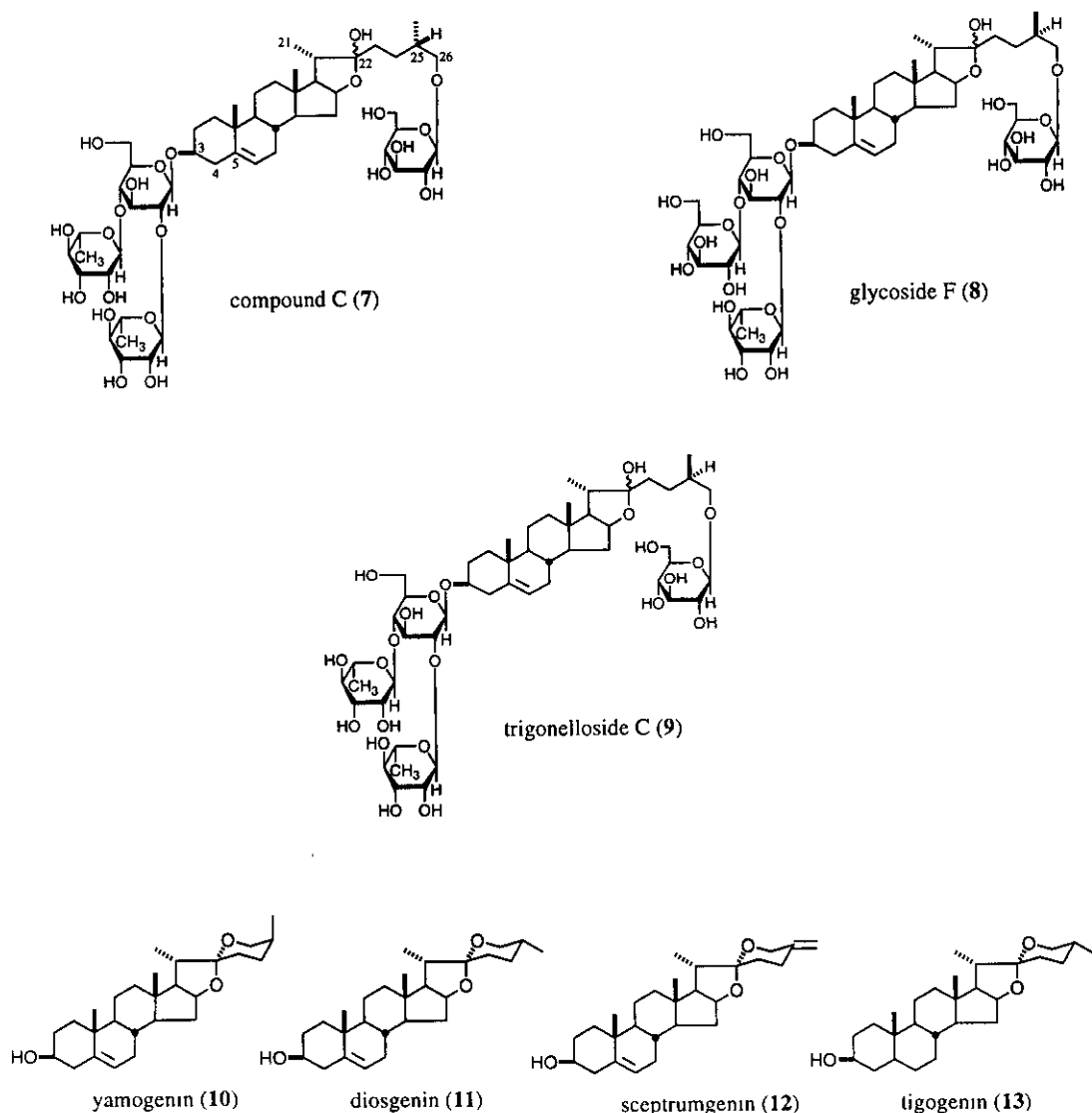
The proton and carbon signals in the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra<sup>10</sup> of **3** were superimposable to those of **2**, except for the proton signals due to the 26-methylene [ $\delta$  3.62 (dd,  $J=6.1, 9.8$  Hz), 3.92 (m)], which showed the 25*R*-configuration.<sup>2</sup> The HMBC experiment of **3** showed long-range correlations between the same protons and carbons as those of **2**. Consequently, the structure of trigoneoside **Vb** was determined to be the 25*R*-isomer (**3**) of trigoneoside **Va** (**2**).

#### Trigoneoside **VI** (**4**), **VIIb** (**5**), and **VIIIb** (**6**)

Trigoneosides **VI** (**4**), **VIIb** (**5**), and **VIIIb** (**6**), isolated as a white powder, were positive in the Ehrlich test. Methanolysis of **4** and **6** liberated sceptrumgenin (**12**)<sup>12</sup> and tigogenin (**13**), respectively, together with methyl glycosides of glucose, rhamnose, and xylose in a *ca.* 5 : 1 : 1 ratio,<sup>9</sup> while **5** liberated diosgenin (**11**) and methyl glycosides of glucose, rhamnose, and xylose



Scheme 1



Scheme 2

in a *ca.* 4 : 1 : 2 ratio<sup>9</sup> by the methanolysis. The molecular formula  $C_{68}H_{110}O_{37}$  of **4** was determined from the negative-ion and positive-ion FABMS and by high-resolution MS measurement. In the positive-ion FABMS of **4**, the quasimolecular ion peak was observed at  $m/z$  1541 ( $M+Na$ )<sup>+</sup>, while the negative-ion FABMS of **4** showed the quasimolecular ion peak at  $m/z$  1517 ( $M-H$ )<sup>-</sup> in addition to fragment ion peaks at  $m/z$  1385 ( $M-C_5H_9O_4$ )<sup>-</sup>,  $m/z$  1355 ( $M-C_6H_{11}O_5$ )<sup>-</sup>,  $m/z$  1061 ( $M-C_{17}H_{29}O_{14}$ )<sup>-</sup>, and  $m/z$  899 ( $M-C_{23}H_{39}O_{19}$ )<sup>-</sup>. The <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) and <sup>13</sup>C-NMR (Table 1) spectra<sup>10</sup> of **4** indicated the presence of the furost-5,25 (27)-diene part [ $\delta$  0.89 (s, 18-H<sub>3</sub>), 1.06 (s, 19-H<sub>3</sub>), 1.33 (d,  $J=6.7$  Hz, 21-H<sub>3</sub>), 4.37, 4.62 (both

Table 1.  $^{13}\text{C}$ -NMR Data of Trigoneosides IVa (1), Va (2), Vb (3), VI (4), VIIb (5), and VIIIb (6)

	1	2	3	4	5	6		1	2	3	4	5	6
C-1	37.5	37.5	37.5	37.4	37.6	37.2	2"	72.4	72.4	72.4	72.3	72.4	72.4
C-2	30.1	30.2	30.1	30.1	30.2	29.9	3"	72.7	72.8	72.7	72.7	72.8	72.8
C-3	78.1	78.2	78.2	78.2	78.3	77.2	4"	74.1	74.1	74.1	74.0	74.2	74.1
C-4	38.9	38.9	38.9	38.9	39.0	34.4	5"	69.5	69.5	69.4	69.4	69.4	69.4
C-5	140.7	140.8	140.8	140.7	140.9	44.6	6"	18.7	18.7	18.6	18.6	18.6	18.7
C-6	121.8	121.8	121.8	121.8	121.8	29.0	Glc-1"	105.2	104.5	104.5	104.4	104.5	104.6
C-7	32.3	32.4	32.3	32.3	32.4	32.5	2"	75.0	73.8	73.7	73.7	73.7	73.8
C-8	31.7	31.7	31.7	31.6	31.8	35.3	3"	78.4	88.1	88.1	88.0	88.5	88.1
C-9	50.3	50.4	50.3	50.3	50.5	54.5	4"	71.2	69.1	69.1	69.0	69.1	69.1
C-10	37.1	37.1	37.1	37.1	37.2	35.9	5"	78.2	77.9	77.8	77.8	77.9	77.9
C-11	21.1	21.1	21.1	21.1	21.2	21.3	6"	61.8	61.4	61.4	61.4	61.6	61.6
C-12	39.9	39.9	39.9	39.9	40.0	40.2	Glc-1"		105.4	105.3	105.3	105.5	105.4
C-13	40.8	40.8	40.8	40.7	40.8	41.1	2"		75.1	75.0	75.0	75.2	75.1
C-14	56.6	56.6	56.6	56.5	56.7	56.4	3"		76.1	76.1	76.0	76.1	76.1
C-15	32.5	32.5	32.5	32.4	32.5	32.4	4"		80.0	80.0	79.9	80.1	80.0
C-16	81.1	81.1	81.1	81.1	81.1	81.1	5"		75.3	75.2	75.1	75.4	75.3
C-17	63.8	63.8	63.8	63.7	63.9	64.0	6"		68.4	68.3	68.3	68.5	68.4
C-18	16.5	16.5	16.4	16.4	16.5	16.7	Xyl-1"		105.3	105.2	105.2	105.2	105.3
C-19	19.4	19.4	19.4	19.3	19.4	12.4	2"		74.9	74.8	74.8	74.8	74.9
C-20	40.7	40.7	40.7	40.6	40.7	40.7	3"		78.4	78.3	78.2	78.2	78.4
C-21	16.5	16.5	16.5	16.3	16.4	16.5	4"		70.9	70.8	70.8	70.9	70.9
C-22	110.7	110.7	110.7	110.3	110.7	110.6	5"		67.3	67.3	67.2	67.3	67.3
C-23	37.1	37.2	37.1	37.9	37.2	37.2	Glc ( or Xyl)-1"		105.0	104.9	104.8	105.5	105.0
C-24	28.3	28.3	28.3	28.3	28.4	28.4	2"		75.4	75.3	75.3	75.1	75.4
C-25	34.4	34.4	34.3	147.2	34.3	34.3	3"		78.3	78.2	78.1	78.4	78.3
C-26	75.4	75.4	75.3	72.0	75.3	75.3	4"		71.5	71.5	71.5	71.7	71.5
C-27	17.4	17.5	17.5	110.7	17.5	17.5	5"		78.3	78.2	78.1	67.1	78.3
Glc-1'	100.0	99.9	99.9	99.9	100.1	99.5	6"		61.6	61.6	61.6		61.6
2'	77.3	77.2	77.2	77.2	77.3	77.5	Glc(26)-1'"	105.1	105.1	104.9	103.8	104.9	104.9
3'	76.2	76.3	76.2	76.1	76.2	76.3	2'"	75.2	75.2	75.1	75.2	75.2	75.2
4'	81.9	81.4	81.4	81.3	81.6	81.6	3'"	78.6	78.6	78.5	78.5	78.6	78.6
5'	77.7	77.6	77.6	77.5	77.6	77.6	4'"	71.6	71.7	71.7	71.6	71.8	71.7
6'	62.1	62.6	62.6	62.5	61.7	62.6	5'"	78.4	78.5	78.4	78.4	78.4	78.5
Rha-1"	101.8	101.8	101.8	101.7	101.8	101.9	6'"	62.8	62.8	62.8	62.7	62.9	62.8

125 MHz, pyridine- $d_5$

m, 26-H<sub>2</sub>), 5.06 (m), 5.34 (br s, 27-H<sub>2</sub>), 5.30 (br s, 6-H)], five  $\beta$ -D-glucopyranosyl moieties [ $\delta$  4.94 (d-like, 1'-H), 5.07 (d,  $J=8.6$  Hz, 1'''-H), 5.21 (d,  $J=7.0$  Hz, 1''''-H), 5.22 (d,  $J=7.0$  Hz, 1'''''-H), 4.89 (d,  $J=7.9$  Hz, 1''''''-H)],  $\alpha$ -L-rhamnopyranosyl moiety [ $\delta$  1.77 (d,  $J=6.1$  Hz, 6''-H<sub>3</sub>), 6.22 (br s, 1''-H)], and  $\beta$ -D-xylopyranosyl moiety [ $\delta$  5.27 (d,  $J=7.7$  Hz, 1''''-H)]. The carbon signals of the saccharide parts in the  $^{13}\text{C}$ -NMR spectrum of **4** were very similar to those of **2** and **3**. Furthermore, in the HMBC experiment of **4**, long-range correlations were observed between the following protons and carbons: 1''''''-H and 6'''-C, 1'''-H and 4'''-C, 1''''-H and 3'''-C, 1'''-H and 4'-C, 1''-H and 2'-C, 1'-H and 3-C, 1''''''-H and 26-C. Those findings led us to formulate the structure of trigoneoside VI as 26-O- $\beta$ -D-glucopyranosyl-furost-5,25(27)-diene-3 $\beta$ ,22 $\xi$ ,26-triol 3-O- $\{\alpha$ -L-rhamnopyranosyl (1 $\rightarrow$ 2) $\}$   $\{[\beta$ -D-xylopyranosyl (1 $\rightarrow$ 4)]  $[\beta$ -D-glucopyranosyl (1 $\rightarrow$ 6)]- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 3)- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 4)]- $\beta$ -D-glucopyranoside (**4**).

The molecular formula C<sub>67</sub>H<sub>110</sub>O<sub>36</sub> of trigoneoside VIIb (**5**) was determined from the quasimolecular ion peaks in their negative-ion [ $m/z$  1489 (M-H)<sup>-</sup>,  $m/z$  1357 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>,  $m/z$  1327 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>,  $m/z$  1063 (M-C<sub>16</sub>H<sub>27</sub>O<sub>13</sub>)<sup>-</sup>] and positive-ion [ $m/z$  1513 (M+Na)<sup>+</sup>] FABMS and by high-resolution MS measurement. The  $^1\text{H}$ -NMR (pyridine-*d*<sub>5</sub>) spectrum<sup>10</sup> of **5** showed signals due to the 25R-furost-5-ene part [ $\delta$  0.90 (s, 18-H<sub>3</sub>), 0.99 (d,  $J=6.8$  Hz, 27-H<sub>3</sub>), 1.05 (s, 19-H<sub>3</sub>), 1.32 (d,  $J=7.0$  Hz, 21-H<sub>3</sub>), 3.62 (dd,  $J=5.8$ , 9.5 Hz), 3.92 (m, 26-H<sub>2</sub>), 3.84 (m, 3-H), 5.30 (br s, 6-H)], four  $\beta$ -D-glucopyranosyl moieties [ $\delta$  4.79 (d,  $J=8.0$  Hz, 1''''''-H), 4.91 (d-like, 1'-H), 5.02 (d,  $J=6.4$  Hz, 1'''-H), 5.04 (d,  $J=7.3$  Hz, 1''''-H)],  $\alpha$ -L-rhamnopyranosyl moiety [ $\delta$  1.74 (d,  $J=6.5$  Hz, 6''-H<sub>3</sub>), 6.17 (br s, 1''-H)], and two  $\beta$ -D-xylopyranosyl moieties [ $\delta$  5.15 (d,  $J=8.6$  Hz, 1''''''-H), 5.25 (d,  $J=7.7$  Hz, 1''''-H)]. The carbon signals of **5** in the  $^{13}\text{C}$ -NMR (Table 1) spectrum<sup>10</sup> was very similar to those of **3**, except for the signals due to terminal  $\beta$ -D-xylopyranosyl moiety. The HMBC experiment of **5** showed long-range correlations between the following protons and carbons: 1''''''-H and 6'''-C, 1'''-H and 4'''-C, 1''''-H and 3'''-C, 1'''-H and 4'-C, 1''-H and 2'-C, 1'-H and 3-C, 1''''''-H and 26-C. On the basis of this evidence, the structure of trigoneoside VIIb (**5**) was clarified as 26-O- $\beta$ -D-glucopyranosyl-(25R)-furost-5-ene-3 $\beta$ ,22 $\xi$ ,26-triol 3-O- $\{\alpha$ -L-rhamnopyranosyl (1 $\rightarrow$ 2) $\}$   $\{[\beta$ -D-xylopyranosyl (1 $\rightarrow$ 4)]  $[\beta$ -D-xylopyranosyl (1 $\rightarrow$ 6)]- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 3)- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 4)]- $\beta$ -D-glucopyranoside (**5**).

Trigoneoside VIIIb (**6**) was found to have the molecular formula C<sub>68</sub>H<sub>114</sub>O<sub>37</sub>, which was determined from the quasimolecular ion peaks in the negative-ion [ $m/z$  1521 (M-H)<sup>-</sup>,  $m/z$  1389 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>,  $m/z$  1359 (M-C<sub>6</sub>H<sub>11</sub>O<sub>4</sub>)<sup>-</sup>,  $m/z$  1065 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>,  $m/z$  903 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup>] and positive-ion [ $m/z$  1545 (M+Na)<sup>+</sup>] FABMS and by high-resolution MS measurement. The  $^1\text{H}$ -NMR (pyridine-*d*<sub>5</sub>) spectrum<sup>10</sup> of **6** indicated the presence of the 26-O- $\beta$ -D-glucopyranosyl-(25R)-5 $\alpha$ -furostanol part [ $\delta$  0.87 (s, 19-H<sub>3</sub>), 0.89 (s, 18-H<sub>3</sub>), 0.99 (d,  $J=6.4$  Hz, 27-H<sub>3</sub>), 1.34 (d,  $J=6.8$  Hz, 21-H<sub>3</sub>), 3.63 (dd,  $J=5.8$ , 9.2 Hz), 3.94 (m, 26-H<sub>2</sub>), 3.92 (m, 3-H)], five  $\beta$ -D-glucopyranosyl moieties [ $\delta$  4.83 (d,  $J=8.0$  Hz, 1''''''-H), 4.97 (d,  $J=7.0$  Hz, 1'-H), 5.08 (d,  $J=7.7$  Hz, 1'''-H), 5.24 (d,  $J=7.9$  Hz, 1''''-H), 5.28 (d,  $J=7.9$  Hz, 1''''''-H)],  $\alpha$ -L-rhamnopyranosyl moiety [ $\delta$  1.76 (d,  $J=6.1$  Hz, 6''-H<sub>3</sub>), 6.22 (br s, 1''-H)], and  $\beta$ -D-xylopyranosyl moiety [ $\delta$  5.32 (d,  $J=7.9$  Hz, 1''''''-H)]. The carbon signals due to the 26-O- $\beta$ -D-glucopyranosyl-(25R)-5 $\alpha$ -furostane-3 $\beta$ ,22 $\xi$ ,26-triol part in the  $^{13}\text{C}$ -NMR (Table 1) spectrum<sup>10</sup> of **6** were superimposable on those of trigoneoside IIIb,<sup>2</sup> whereas the carbon signals due to the oligoglycoside at the 3-position resembled to those of **2**, **3**, and **4**. Finally, the HMBC experiment of **6** led us to formulate the structure of trigoneoside VIIIb as 26-O- $\beta$ -D-glucopyranosyl-(25R)-5 $\alpha$ -furostane-3 $\beta$ ,22 $\xi$ ,26-triol 3-O- $\{\alpha$ -L-rhamnopyranosyl (1 $\rightarrow$ 2) $\}$   $\{[\beta$ -D-xylopyranosyl (1 $\rightarrow$ 4)]  $[\beta$ -D-glucopyranosyl (1 $\rightarrow$ 6)]- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 3)- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 4)]- $\beta$ -D-glucopyranoside (**6**).

## EXPERIMENTAL

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper<sup>13</sup>

### Isolation of Trigoneosides IVa (1), Va (2), Vb (3), VI (4), VIIb (5), VIIIb (6), and IX and Known Compounds (7, 8, 9)

Fractions 2-5 (1.6 g, 0.059%), 5 (36.2 g, 1.4%), 6 (11.5 g, 0.44%), and 7 (26.7 g, 1.02%) were obtained from the seeds of *Trigonella foenum-graecum* L. (10 kg, cultivated in India and purchased from Honso Pharmaceutical Co., Ltd., Nagoya) as reported previously.<sup>1</sup> Fractions 2-5 (1.6 g) were purified by HPLC [YMC-Pack ODS-A (YMC Co., Ltd., 250 x 20 mm i.d.), MeCN-H<sub>2</sub>O (35 : 65, v/v)] to give trigoneoside IX (271 mg, 0.010%). Fraction 5 (36.2 g) was separated by HPLC [MeCN-H<sub>2</sub>O (25 : 75, v/v)] to give trigoneoside IVa (1, 4339 mg, 0.16%), glycoside F (8, 8136 mg, 0.30%), compound C (7, 9492 mg, 0.35%), and trigonelloside C (9, 4068 mg, 0.15%). Fractions 6 (11.5 g) and 7 (26.7 g) were separated by HPLC [MeCN-H<sub>2</sub>O (25 : 75, v/v)] to give trigoneosides Va (2, 6508 mg, 0.24%), Vb (3, 8949 mg, 0.33%), and VI (4, 1790 mg, 0.066%) and crude saponin fraction (2712 mg). Crude saponin fraction (2712 mg) was separated by HPLC [1) YMC-Pack ODS-AL (YMC Co., Ltd., 250 x 20 mm i.d.), MeCN-H<sub>2</sub>O (25 : 75, v/v); 2) YMC-Pack ODS-A (YMC Co., Ltd., 250 x 20 mm i.d.), MeOH-H<sub>2</sub>O (60 : 40, v/v)] to give 22-methoxytrigoneosides VIIb (461 mg, 0.017%) and VIIIb (407 mg, 0.015%). 22-Methoxytrigoneosides VIIb (461 mg) and VIIIb (407 mg) in MeCN-H<sub>2</sub>O (10 mL, 1 : 1, v/v) were stirred under reflux for 3 h to give trigoneosides VIIb (quant.) and VIIIb (quant.). The known compounds (7-9) were identified by comparison of their physical data ([ $\alpha$ ]<sub>D</sub>, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR) with reported values.<sup>3-5</sup>

Trigoneoside IVa (1) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>28</sup> -56.5° (c=0.8, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>51</sub>H<sub>84</sub>O<sub>23</sub>Na (M+Na)<sup>+</sup> : 1087.5301; Found : 1087.5320. IR (KBr, cm<sup>-1</sup>) : 3410, 2934, 1072, 1052. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.90 (3H, s, 18-H<sub>3</sub>), 1.03 (3H, d, *J*=6.7 Hz, 27-H<sub>3</sub>), 1.06 (3H, s, 19-H<sub>3</sub>), 1.33 (3H, d, *J*=7.1 Hz, 21-H<sub>3</sub>), 1.77 (3H, d, *J*=6.4 Hz, Rha-6-H<sub>3</sub>), 2.24 (1H, dq, *J*=6.9, 6.9 Hz, 20-H), 3.49 (1H, dd, *J*=7.1, 9.5 Hz), 4.09 (1H, dd, *J*=6.1, 9.5 Hz, 26-H<sub>2</sub>), 3.88 (1H, m, 3-H), 4.82 (1H, d, *J*=8.0 Hz, Glc-1'''-H), 4.95 (1H, d, *J*=9.0 Hz, Glc-1'-H), 5.14 (1H, d, *J*=8.0 Hz, Glc-1''-H), 5.29 (1H, d-like, 6-H), 6.26 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS (*m/z*) : 1063 (M-H)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1087 (M+Na)<sup>+</sup>.

Trigoneoside Va (2) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>26</sup> -53.8° (c=0.3, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>68</sub>H<sub>112</sub>O<sub>37</sub>Na (M+Na)<sup>+</sup> : 1543.6780; Found : 1543.6730. IR (KBr, cm<sup>-1</sup>) : 3400, 2931, 1159, 1074, 1044. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.90 (3H, s, 18-H<sub>3</sub>), 1.04 (3H, d, *J*=6.7 Hz, 27-H<sub>3</sub>), 1.07 (3H, s, 19-H<sub>3</sub>), 1.33 (3H, d, *J*=6.7 Hz, 21-H<sub>3</sub>), 1.78 (3H, d, *J*=6.1 Hz, Rha-6''-H<sub>3</sub>), 2.24 (1H, dq, *J*=7.0, 7.0 Hz, 20-H), 3.50 (1H, dd, *J*=7.1, 9.2 Hz), 4.09 (1H, m, 26-H<sub>2</sub>), 3.88 (1H, m, 3-H), 4.83 (1H, d, *J*=7.7 Hz, Glc-1'''''-H), 4.95 (1H, d-like, Glc-1'-H), 5.08 (1H, d-like, Glc-1'''-H), 5.24 (1H, d, *J*=8.0 Hz, Glc-1''''-H), 5.28 (1H, d, *J*=8.0 Hz, Glc-1'''''-H), 5.29 (1H, br s, 6-H), 5.33 (1H, d, *J*=7.6 Hz, Xyl-1'''''-H), 6.25 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS (*m/z*) : 1519 (M-H)<sup>-</sup>, 1387 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>, 1357 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>, 1063 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>, 901 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1543 (M+Na)<sup>+</sup>.

Trigoneoside Vb (3) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -55.6° (c=0.5, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>68</sub>H<sub>112</sub>O<sub>37</sub>Na (M+Na)<sup>+</sup> : 1543.6780; Found : 1543.6868. IR (KBr, cm<sup>-1</sup>) : 3400, 2934, 1159, 1074, 1050. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.90 (3H, s, 18-H<sub>3</sub>), 0.99 (3H, d, *J*=6.4 Hz, 27-H<sub>3</sub>), 1.06 (3H, s, 19-H<sub>3</sub>), 1.34 (3H, d, *J*=6.8 Hz, 21-H<sub>3</sub>), 1.77 (3H, d, *J*=6.4 Hz, Rha-6''-H<sub>3</sub>), 2.25 (1H, dq, *J*=7.0, 7.0 Hz, 20-H), 3.62 (1H, dd, *J*=6.1, 9.8 Hz), 3.92 (1H, m, 26-H<sub>2</sub>), 3.88 (1H, m, 3-H), 4.81 (1H, d, *J*=7.9 Hz, Glc-1'''''-H), 4.95 (1H, d, *J*=6.7 Hz, Glc-1'-H), 5.08 (1H, d, *J*=8.6 Hz, Glc-1'''-H), 5.22 (1H, d, *J*=9.2 Hz, Glc-1''''-H), 5.23 (1H, d, *J*=8.0 Hz, Glc-1'''''-H), 5.28 (1H, d, *J*=8.0 Hz, Xyl-1'''''-H), 5.30 (1H, br s, 6-H), 6.22 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS

(*m/z*) : 1519 (M-H)<sup>-</sup>, 1387 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>, 1357 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>, 1063 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>, 901 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1543 (M+Na)<sup>+</sup>.

Trigoneoside VI (4) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>26</sup> -54.7° (*c*=0.3, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>68</sub>H<sub>110</sub>O<sub>37</sub>Na (M+Na)<sup>+</sup> : 1541.6623; Found : 1541.6667. IR (KBr, cm<sup>-1</sup>) : 3404, 2932, 1655, 1159, 1073, 1044. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.89 (3H, s, 18-H<sub>3</sub>), 1.06 (3H, s, 19-H<sub>3</sub>), 1.33 (3H, d, *J*=6.7 Hz, 21-H<sub>3</sub>), 1.77 (3H, d, *J*=6.1 Hz, Rha-6"-H<sub>3</sub>), 2.26 (1H, m, 20-H), 3.87 (1H, m, 3-H), 4.37, 4.62 (1H each, both m, 26-H<sub>2</sub>), 4.89 (1H, d, *J*=7.9 Hz, Glc-1''''-H), 4.94 (1H, d-like, Glc-1'-H), 5.06 (1H, m), 5.34 (1H, br s, 27-H<sub>2</sub>), 5.07 (1H, d, *J*=8.6 Hz, Glc-1'''-H), 5.21 (1H, d, *J*=7.0 Hz, Glc-1''-H), 5.22 (1H, d, *J*=7.0 Hz, Glc-1''''-H), 5.27 (1H, d, *J*=7.7 Hz, Xyl-1''''-H), 5.30 (1H, br s, 6-H), 6.22 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS (*m/z*) : 1517 (M-H)<sup>-</sup>, 1385 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>, 1355 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>, 1061 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>, 899 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1541 (M+Na)<sup>+</sup>.

Trigoneoside VIIb (5) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>27</sup> -55.9° (*c*=1.7, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>67</sub>H<sub>110</sub>O<sub>36</sub>Na (M+Na)<sup>+</sup> : 1513.6675; Found : 1513.6665. IR (KBr, cm<sup>-1</sup>) : 3409, 2930, 1161, 1071, 1044. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.90 (3H, s, 18-H<sub>3</sub>), 0.99 (3H, d, *J*=6.8 Hz, 27-H<sub>3</sub>), 1.05 (3H, s, 19-H<sub>3</sub>), 1.32 (3H, d, *J*=7.0 Hz, 21-H<sub>3</sub>), 1.74 (3H, d, *J*=6.5 Hz, Rha-6"-H<sub>3</sub>), 2.24 (1H, dq, *J*=6.4, 6.4 Hz, 20-H), 3.62 (1H, dd, *J*=5.8, 9.5 Hz), 3.92 (1H, m, 26-H<sub>2</sub>), 3.84 (1H, m, 3-H), 4.79 (1H, d, *J*=8.0 Hz, Glc-1''''-H), 4.91 (1H, d-like, Glc-1'-H), 5.02 (1H, d, *J*=6.4 Hz, Glc-1'''-H), 5.04 (1H, d, *J*=7.3 Hz, Glc-1''-H), 5.15 (1H, d, *J*=8.6 Hz, Xyl-1''''-H), 5.25 (1H, d, *J*=7.7 Hz, Xyl-1''''-H), 5.30 (1H, br s, 6-H), 6.17 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS (*m/z*) : 1489 (M-H)<sup>-</sup>, 1357 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>, 1327 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>, 1063 (M-C<sub>16</sub>H<sub>27</sub>O<sub>13</sub>)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1513 (M+Na)<sup>+</sup>.

Trigoneoside VIIIb (6) : a white powder, [ $\alpha$ ]<sub>D</sub><sup>23</sup> -44.0° (*c*=0.3, pyridine). High-resolution positive-ion FABMS (*m/z*) : Calcd for C<sub>68</sub>H<sub>114</sub>O<sub>37</sub>Na (M+Na)<sup>+</sup> : 1545.6937; Found : 1545.6923. IR (KBr, cm<sup>-1</sup>) : 3416, 2932, 1073, 1044. <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>, 500 MHz,  $\delta$ ) : 0.87 (3H, s, 18-H<sub>3</sub>), 0.89 (3H, s, 19-H<sub>3</sub>), 0.99 (3H, d, *J*=6.4 Hz, 27-H<sub>3</sub>), 1.34 (3H, d, *J*=6.8 Hz, 21-H<sub>3</sub>), 1.76 (3H, d, *J*=6.1 Hz, Rha-6"-H<sub>3</sub>), 2.24 (1H, dq, *J*=6.8, 6.8 Hz, 20-H), 3.63 (1H, dd, *J*=5.8, 9.2 Hz), 3.94 (1H, m, 26-H<sub>2</sub>), 3.92 (1H, m, 3-H), 4.83 (1H, d, *J*=8.0 Hz, Glc-1''''-H), 4.97 (1H, d, *J*=7.0 Hz, Glc-1'-H), 5.08 (1H, d, *J*=7.7 Hz, Glc-1'''-H), 5.24 (1H, d, *J*=7.9 Hz, Glc-1''-H), 5.28 (1H, d, *J*=7.9 Hz, Glc-1''''-H), 5.32 (1H, d, *J*=7.9 Hz, Xyl-1''''-H), 6.22 (1H, br s, Rha-1''-H). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>, 125 MHz,  $\delta$ <sub>C</sub>) : given in Table 1. Negative-ion FABMS (*m/z*) : 1521 (M-H)<sup>-</sup>, 1389 (M-C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>)<sup>-</sup>, 1359 (M-C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>)<sup>-</sup>, 1065 (M-C<sub>17</sub>H<sub>29</sub>O<sub>14</sub>)<sup>-</sup>, 903 (M-C<sub>23</sub>H<sub>39</sub>O<sub>19</sub>)<sup>-</sup>. Positive-ion FABMS (*m/z*) : 1545 (M+Na)<sup>+</sup>.

#### Methanolysis of Trigoneosides IVa (1), Va (2), Vb (3), VI (4), VIIb (5), and VIIIb (6)

A solution of trigoneosides (1-6, 5 mg each) in 9% HCl-MeOH (0.5 mL) was heated under reflux for 2.5 h. After cooling, the reaction mixture was neutralized with Ag<sub>2</sub>CO<sub>3</sub> powder and the insoluble portion was removed by filtration. Each product, which was obtained from the filtrate by removal of the solvent under reduced pressure, was purified by reversed-phase silica gel column chromatography [Chromatorex ODS (Fuji Silysia Chemical Ltd., 0.5 g), MeOH-H<sub>2</sub>O (80 : 20, v/v)] to give the sapogenol constituent [yamogenin (10, 0.6 mg, 30.5%) from 1, 10 (0.7 mg, 50.8 %) from 2, diosgenin (11, 1.0 mg, 50.8 %) from 3, sceptorugenin (12, 0.9 mg, 64.6%) from 4, 11 (0.7 mg, 50.6 %) from 5, tigogenin (13, 0.7 mg, 51.5%) from 6]. 10, 11, 12, and 13 was identified by comparison of melting point, [ $\alpha$ ]<sub>D</sub>, and <sup>1</sup>H-NMR data with reported values.<sup>5b,8,11,14</sup> The sugar composition of the product was analyzed by GLC. A solution of each product in pyridine (0.02



mL) was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.01 mL) for 1 h. The reaction solution was then subjected to GLC analysis to identify trimethylsilyl (TMS) derivatives of methyl glycosides [methyl glucoside (i) and methyl rhamnoside (ii) from **1**, i, ii, and methyl xyloside (iii) from **2**, **3**, **4**, **5**, and **6**]. GLC conditions : CBR-M25-025, 0.25 mm (i.d.) x 25 m capillary column; column temperature : 140-280 °C, He flow rate 15 mL/min,  $t_R$  : i (17.9, 18.2, 19.3 min), ii (12.3, 12.7 min), iii (13.9, 14.3 min).

#### Acid Hydrolysis of Trigoneoside Vb (**3**)

A solution of trigoneoside Vb (**3**, 2 mg) in 5% aqueous H<sub>2</sub>SO<sub>4</sub>-1,4-dioxane (1 mL, 1 : 1, v/v) was heated under reflux for 1 h. After cooling, the reaction solution was neutralized Amberlite IRA-400 (OH<sup>-</sup> form) and the resin was removed by filtration. After removal of the solvent from the filtrate under reduced pressure, the residue was separated on a Sep-Pack C<sub>18</sub> cartridge column (H<sub>2</sub>O→MeOH). The H<sub>2</sub>O eluate was concentrated under reduced pressure to give a residue, which was treated with L-cysteine methyl ester hydrochloride (2 mg) in pyridine (0.02 mL) and the mixture was left standing at 60 °C for 1 h. The reaction solution was then treated with BSTFA (0.01 mL) and the whole mixture was subjected to GLC analysis to identify the trimethylsilyl thiazolidine derivatives of D-glucose (i), L-rhamnose (ii), and D-xylose (iii). GLC conditions : column, Supelco SPB<sup>TM</sup>-1, 0.25 mm (i.d.) x 30 m; column temperature, 230 °C;  $t_R$ , i, 24.2 min; ii, 15.4 min; iii, 13.8 min.

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