Medicinal Foodstuffs. XVII.[1] Fenugreek Seed. (3): Structures of New Furostanol-Type Steroid Saponins, Trigoneosides Xa, Xb, XIb, XIIa, XIIb, and XIIIa, from the Seeds of Egyptian *Trigonella foenum-graecum* L.

Toshiyuki MURAKAMI, Akinobu KISHI, Hisashi MATSUDA, and Masayuki YOSHIKAWA*

Kyoto Pharmaceutical University, Misasagi, Yamashina-ku, Kyoto 607–8414, Japan.
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Six new furostanol-type steroid saponins called trigoneosides Xa, Xb, XIb, XIIa, XIIb, and XIIIa were isolated from the seeds of Egyptian *Trigonella foenum-graecum* L. (Leguminosae) together with six known furostanol-type steroid saponins: trigoneosides Ia, Ib, and Va, glycoside D, trigonelloside C, and compound C. The structures of trigoneosides Xa, Xb, XIb, XIIa, XIIb, and XIIIa were determined on the basis of chemical and physicochemical evidence as 26-*O*-β-D-glucopyranosyl-(25*S*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside, 26-*O*-β-D-glucopyranosyl-(25*R*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside, 26-*O*-β-D-glucopyranosyl-(25*R*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-β-D-xylopyranosyl(1→4)-β-D-glucopyranoside, 26-*O*-β-D-glucopyranosyl-(25*S*)-furost-4-ene-3β,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside, 26-*O*-β-D-glucopyranosyl-(25*R*)-furost-4-ene-3β,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside, and 26-*O*-β-D-glucopyranosyl-(25*S*)-furost-5-ene-3β,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)-β-D-glucopyranosyl(1→4)]-β-D-glucopyranoside, respectively.

Key words *Trigonella foenum-graecum*; trigoneosides Xa—XIIIa; fenugreek; furostanol-type steroid saponin; adjuvant activity; trigonegenin A—B

Fenugreek (*Trigonella foenum-graecum* L., Leguminosae) has been widely cultivated in India, China, and Mediterranean countries. From ancient times, the seeds of this plant have been used not only as a spice or favorite food but also an antipyretic, laxative, and strengthening agent. In Chinese traditional medicine, the seeds (Japanese and Chinese name "胡蘆巴") have been prescribed for tonic and stomachic purposes. In the course of our characterization studies on the bioactive constituents of medicinal foodstuffs,[1,2] we have reported the isolation of thirteen furostanol-type steroid saponins called trigoneosides Ia (**7**), Ib (**8**), IIa, IIb, IIIa, IIIb, IVa, Va (**12**), Vb, VI, VIIb, VIIIb, and IX from Indian fenugreek seeds and their structure elucidations.[3] Furthermore, we have examined the adjuvant and haemolytic activities of the saponin constituents from Indian fenugreek seeds. Among the saponin constituents, trigoneosides Ia (**7**), IIa, IIb, Va (**12**), and VI were found to show the antibody response in mice, but no haemolytic activity. Particularly, trigoneoside VI showed the potent adjuvant activity, which was stronger than quillaja saponin (QS-21).[4] As part of our continuing studies on fenugreek seeds, we have isolated six new furostanol-type steroid saponins called trigoneosides Xa (**1**), Xb (**2**), XIb (**3**), XIIa (**4**), XIIb (**5**), and XIIIa (**6**) from Egyptian fenugreek seeds. In this paper, we describe the structure elucidation of these trigoneosides (**1**—**6**) on the basis of chemical and physicochemical evidence.

The steroid saponin constituents of Egyptian fenugreek seeds were separated by the procedures shown in Chart 1. Thus, the methanolic extract from the seeds was subjected to Diaion HP-20 column chromatography to give the water-, the methanol-, and the acetone-eluted fractions. Next, the methanol-eluted fraction was separated with ordinary- and reversed-phase silica gel column chromatography and finally HPLC to afford trigoneosides Xa (**1**, 0.038%), Xb (**2**, 0.031%), XIb (**3**, 0.0026%), XIIa (**4**, 0.0071%), XIIb (**5**, 0.0059%), and XIIIa (**6**, 0.0075%) together with trigoneosides Ia[3] (**7**, 0.0095%), Ib[3] (**8**, 0.010%), and Va[3] (**12**, 0.030%), glycoside D[5] (**9**, 0.023%), trigonelloside C[6] (**10**, 0.0073%), and compound C[7] (**11**, 0.021%).

Trigoneoside Xa (**1**) was obtained as a white powder and was deduced to possess a furostanol structure based on TLC examination using the Ehrlich reagent.[8] The IR spectrum of **1** showed absorption bands at 3432, 1072, and 1044 cm^{-1} suggestive of oligoglycosidic structure. In the negative- and positive-ion FAB-MS of **1**, quasimolecular ion peaks were observed at *m/z* 919 $(M-H)^-$ and *m/z* 943 $(M+Na)^+$, respectively, and high-resolution MS analysis revealed the

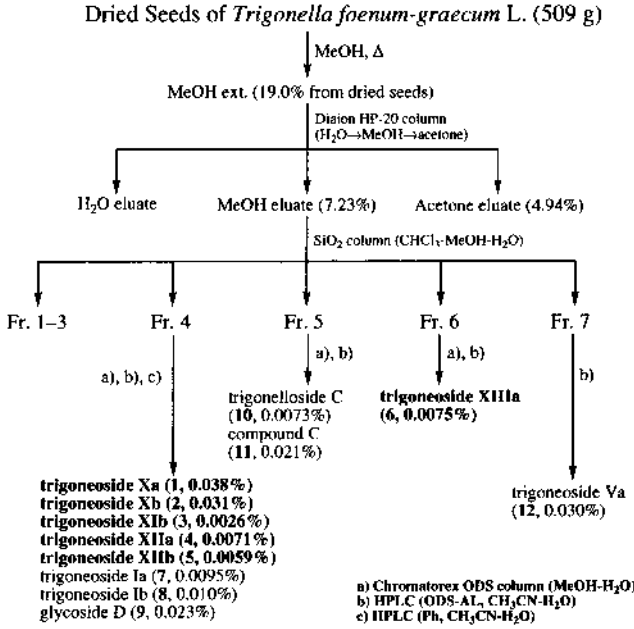

Chart 1

* To whom correspondence should be addressed. e-mail: shoyaku@mb.kyoto-phu.ac.jp

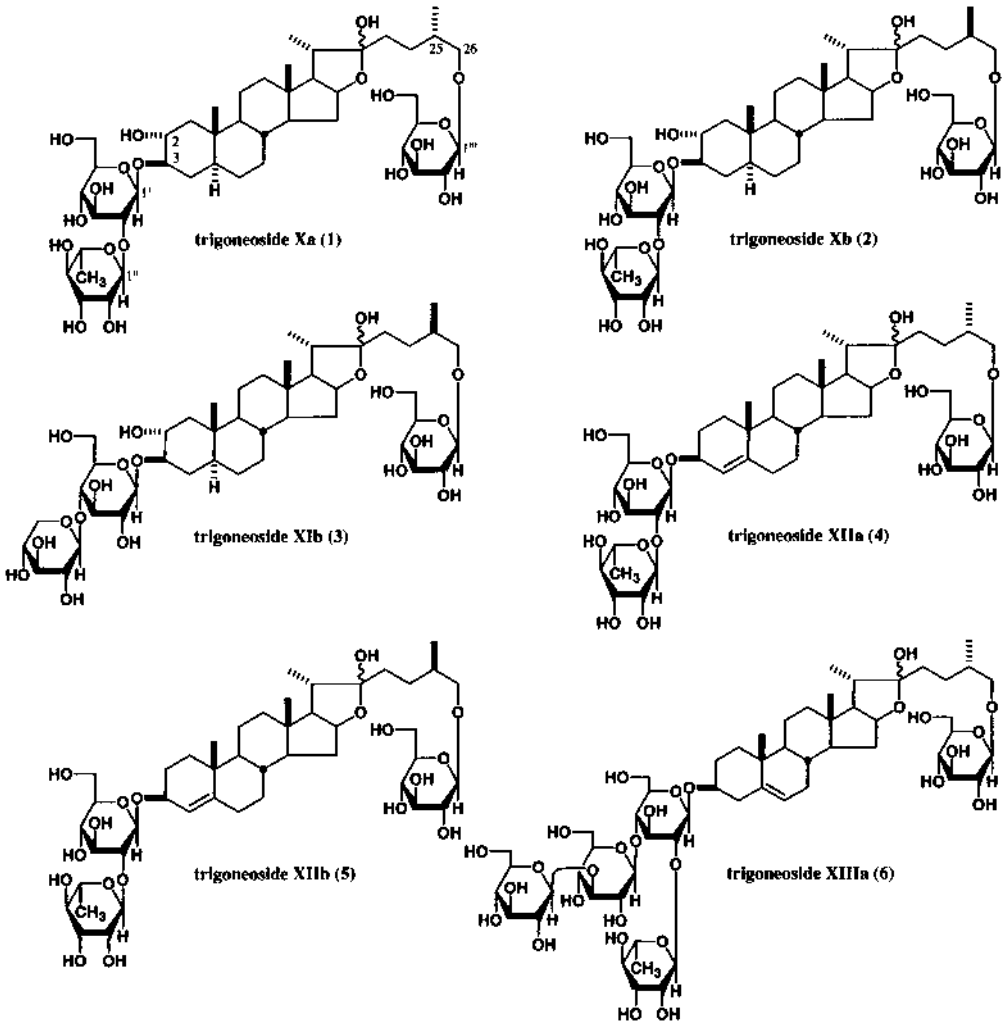

Chart 2

molecular formula of **1** to be $C_{45}H_{76}O_{19}$. Furthermore, fragment ion peaks at *m/z* 773 $(M-C_6H_{11}O_4)^-$, *m/z* 757 $(M-C_6H_{11}O_5)^-$, *m/z* 611 $(M-C_{12}H_{21}O_9)^-$, and *m/z* 449 $(M-C_{18}H_{31}O_{14})^-$, which were derived by cleavage of the glycosidic linkage at the terminal deoxyhexose, hexose, and their diglycoside moieties, respectively, were observed in the negative-ion FAB-MS of **1**. Acid hydrolysis of **1** with 2 N hydrochloric acid (HCl)–1,4-dioxane (1 : 1, v/v) furnished neogitogenin (**13**)[9] having 25*S*-configuration and gitogenin (**14**)[10] having 25*R*-configuration in a 2 : 1 ratio. On the other hand, D-glucose and L-rhamnose, which were identified by GLC analysis of the thiazolidine derivative,[11] were obtained on acid hydrolysis of **1** with 5% aqueous sulfuric acid (H_2SO_4)–1,4-dioxane (1 : 1, v/v). Since 25*S*-steroidal aglycones were known to change to 25*R*-steroidal aglycones with acid treatment,[3] the configuration at the 25-position of **1** was deduced to be *S*.

The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1**, which were assigned by various NMR analytical methods,[12] showed signals assignable to a 5α-frostane-2α,3β,22ξ,26-tetraol part [δ 0.86, 0.88 (both s, 18, 19-H$_3$), 1.01 (d, J=6.2 Hz, 27-H$_3$), 1.28 (d, J=6.6 Hz, 21-H$_3$), 3.47 (dd-like), 4.06 (m) (26-H$_2$), 3.86 (m, 3-H), 4.08 (m, 2-H), 4.90 (m, 16-H)], 3-*O*-β-D-glucopyranosyl moiety [δ 5.01 (d, J=7.0 Hz, 1′-H)], 2′-*O*-α-L-rhamnopyranosyl moiety [δ 1.67 (d, J=5.6 Hz, 6″-H$_3$), 6.27 (br s, 1″-H)], and 26-*O*-β-D-glucopyranosyl moiety [δ 4.76 (d, J=8.2 Hz, 1‴-H)]. The 25*S*-configuration of **1** was confirmed by comparison of the 26-methylene signals for **1** with those for **7** and **8** in the ^{1}H-NMR spectrum.[3] The carbon signals due to the sapogenol moiety in the ^{13}C-NMR spectrum of **1** were superimposable on those of trigoneosides Ia (**7**) and IIa (**8**) having 5α-frostane-2α,3β,22ξ,26-tetraol 3,26-glycosidic structure.[3] The 3,26-bisdesmoside structure of **1** was characterized by a heteronuclear multiple bond correlation (HMBC) experiment. Namely, long-range correlations were observed between the 1′-proton and the 3-carbon, between the 1″-proton and the 2′-carbon, and between the 1‴-proton and the 26-carbon. Consequently, the structure of trigoneoside Xa was elucidated to be 26-*O*-β-D-glucopyranosyl-(25*S*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-α-L-rhamnopyranosyl-(1$\rightarrow$2)-β-D-glucopyranoside (**1**).

Trigoneoside Xb (**2**), isolated as a white powder, was also deduced to possess a furostanol structure by the Ehrlich test. The IR spectrum of **2** was found similar to that of **1**. The negative- and positive-ion FAB-MS of **2** showed quasimolecular ion peaks at *m/z* 919 $(M-H)^-$ and *m/z* 943 $(M+Na)^+$, respectively, and fragment ion peaks at *m/z* 773

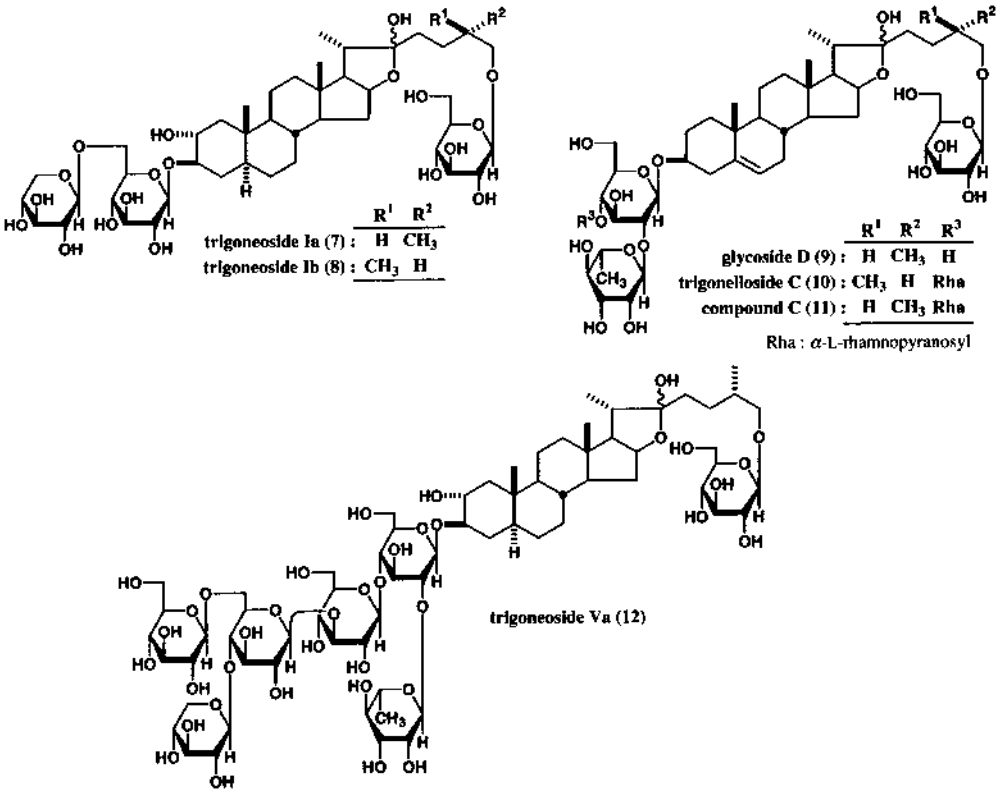

Chart 3

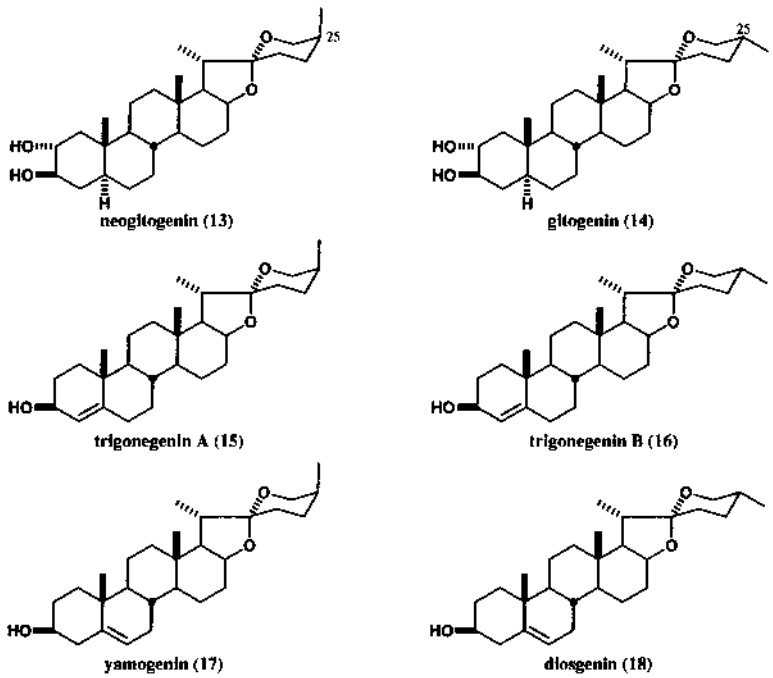

Chart 4

$(M-C_6H_{11}O_4)^-$, 757 $(M-C_6H_{11}O_5)^-$, 611 $(M-C_{12}H_{21}O_9)^-$, and 449 $(M-C_{18}H_{31}O_{14})^-$ were observed in the negative-ion FAB-MS of **2**. High-resolution MS analysis revealed the molecular formula of **2** to be $C_{45}H_{76}O_{19}$, which was the same as that of **1**. Acid hydrolysis of **2** with 2 N HCl–dioxane liberated gitogenin (**14**), while acid hydrolysis of **2** with 5% aqueous H_2SO_4–dioxane furnished D-glucose and L-rhamnose.[11] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[12] of **2** were shown to be superimposable on those of **1**, except for the 26-protons [δ 3.61 (dd, J=6.4, 9.2 Hz), 3.96 (m)], which showed the 25*R*-configuration.[3] The 3,26-bisdesmoside structure of **2** was identified by a HMBC experiment, in which long-range correlations were observed between the 1″-proton and the 2′-carbon, between the 1′-proton and 3-

Table 1. ^{13}C-NMR Data for **1**—**6**, **15** and **16**

	1[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**15**[b]	**16**[b]		**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]
C-1	45.8	45.8	45.8	35.8	35.8	37.6	35.4	35.4	C-1′	101.4	101.4	105.6	101.7	101.6	100.1
C-2	70.7	70.7	70.5	27.8	27.8	30.2	29.5	29.5	C-2′	78.1	78.1	74.7	78.2	78.3	77.3
C-3	85.6	85.6	85.2	75.5	75.5	78.4	67.9	67.9	C-3′	78.3	78.2	76.5	78.6	78.6	76.2
C-4	33.7	33.7	34.0	121.5	121.5	39.0	123.5	123.5	C-4′	71.9	72.0	80.9	72.1	72.0	81.5
C-5	44.7	44.8	44.8	147.2	147.3	140.9	147.4	147.4	C-5′	79.4	79.5	76.6	79.7	79.6	77.6
C-6	28.2	28.2	28.2	33.5	32.5	121.8	32.1	32.1	C-6′	62.6	62.6	61.8	62.9	62.9	61.7
C-7	32.3	32.3	32.3	32.6	33.5	32.4	33.2	33.2	C-1″	102.1	102.1	103.0	102.3	102.3	101.7
C-8	34.4	34.3	34.7	36.0	35.8	31.8	35.5	35.5	C-2″	72.4	72.4	75.0	72.5	72.6	72.4
C-9	54.5	54.5	54.6	54.7	54.7	50.5	54.4	54.4	C-3″	72.7	72.8	78.4	72.8	72.8	72.8
C-10	36.9	36.9	37.0	37.7	37.7	37.2	37.4	37.4	C-4″	74.1	74.1	70.8	74.1	74.1	74.2
C-11	21.5	21.5	21.5	21.1	21.1	21.2	20.9	20.8	C-5″	69.4	69.4	67.4	69.5	69.4	69.4
C-12	40.2	40.2	40.2	40.2	40.2	40.0	39.9	39.9	C-6″	18.5	18.8		18.6	18.6	18.6
C-13	41.1	41.2	41.2	41.1	41.1	40.8	40.4	40.4	C-1″	105.0	104.9	104.9	105.1	104.9	104.5
C-14	56.3	56.4	56.4	56.2	56.2	56.7	56.0	56.0	C-2″	75.1	75.2	75.2	75.2	75.2	73.7
C-15	32.3	32.4	32.4	32.4	32.4	32.5	31.8	31.8	C-3″	78.5	78.5	78.6	78.5	78.6	88.3
C-16	81.1	81.1	81.2	81.1	81.1	81.2	80.8	80.8	C-4″	71.8	71.8	71.9	71.8	71.7	69.4
C-17	63.9	64.0	64.0	63.9	63.9	63.9	62.1	62.1	C-5″	78.2	78.2	78.4	78.3	78.4	78.4
C-18	16.7	16.7	16.7	16.7	16.7	16.5	16.3	16.4	C-6″	62.9	62.9	63.0	62.9	62.9	61.8
C-19	13.5	13.5	13.5	18.9	18.9	19.4	18.9	19.0	C-1‴						105.8
C-20	40.7	40.7	40.7	40.8	40.7	40.7	42.1	41.6	C-2‴						75.2
C-21	16.4	16.3	16.4	16.4	16.4	16.4	14.3	14.5	C-3‴						78.3
C-22	110.6	110.6	110.7	110.7	110.7	110.7	109.7	109.2	C-4‴						71.8
C-23	37.1	37.1	37.2	37.1	37.2	37.2	25.9	31.4	C-5‴						78.6
C-24	28.4	28.4	28.4	28.3	28.4	28.3	25.8	28.8	C-6‴						62.6
C-25	34.7	34.7	34.3	34.4	34.3	34.4	27.1	30.3	C-1⁗						105.1
C-26	75.3	75.2	75.2	75.3	75.3	75.5	65.1	66.8	C-2⁗						75.2
C-27	17.4	17.4	17.5	17.5	17.5	17.4	16.1	17.1	C-3⁗						78.6
									C-4⁗						71.7
									C-5⁗						78.4
									C-6⁗						62.9

a) Pyridine-d_5, *b*) $CDCl_3$.

carbon, and between the 1‴-proton and the 26-carbon. Finally, by comparison of the NMR data for **2** with those for related furostanol saponins,[3] the structure of trigoneoside Xb was determined to be 26-*O*-β-D-glucopyranosyl-(25*R*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside (**2**).

Trigoneoside XIb (**3**), isolated as a white powder, was positive in the Ehrlich test. Acid hydrolysis of **3** with 5% aqueous H_2SO_4–dioxane liberated D-glucose and D-xylose,[11] while gitogenin (**14**) was obtained by acid hydrolysis of **3** with 2 N HCl–dioxane. The molecular formula $C_{44}H_{74}O_{19}Na$ of **3** was determined from the negative- and positive-ion FAB-MS and by high-resolution MS measurement. In the positive-ion FAB-MS of **3**, the quasimolecular ion peak was observed at *m/z* 929 $(M+Na)^+$, while the negative-ion FAB-MS of **3** showed the quasimolecular ion peak at *m/z* 905 $(M-H)^-$ in addition to fragment ion peaks at *m/z* 773 $(M-C_5H_9O_4)^-$ and *m/z* 611 $(M-C_{11}H_{19}O_9)^-$. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[12] of **3** indicated the presence of a (25*R*)-5α-furostane-2α,3β,22ξ,26-tetraol part [δ 0.75, 0.87 (both s, 19, 18-H$_3$), 0.99 (d, J=6.7 Hz, 27-H$_3$), 1.31 (d, J=7.0 Hz, 21-H$_3$), 3.62, 3.93 (both m, 26-H$_2$), 3.84 (m, 3-H), 3.95 (m, 2-H), 4.92 (ddd-like, 16-H)], two β-D-glucopyranosyl parts [δ 5.01 (d, J=7.6 Hz, 1′-H), 4.79 (d, J=7.6 Hz, 1‴-H)], and a β-D-xylopyranosyl part [δ 5.10 (d, J=7.3 Hz, 1″-H)]. The carbon signals in the ^{13}C-NMR spectrum of **3** were very similar to those of **2** except for the 3-*O*-oligoglycoside structure. In the HMBC experiment of **3**, long-range correlations were observed between the following protons and carbons: 1″-H and 4′-C, 1′-H and 3-C, 1‴-H and 26-C. Those findings led us to formulate the structure of trigoneoside XIb as 26-*O*-β-D-glucopyranosyl-(25*R*)-5α-furostane-2α,3β,22ξ,26-tetraol 3-*O*-β-D-xylopyranosyl(1→4)-β-D-glucopyranoside (**3**).

Trigoneosides XIIa (**4**) and XIIb (**5**), which were each isolated as a white powder, were positive in an Ehrlich test.[7] The IR spectra of **4** and **5** showed absorption bands due to hydroxyl groups. Trigoneosides XIIa (**4**) and XIIb (**5**) were found to have the same molecular formula $C_{45}H_{74}O_{18}$, which was determined from their negative- and positive-ion FAB-MS and by high-resolution MS measurement. Thus, in the positive-ion FAB-MS of **4** and **5**, the quasimolecular ion peak was observed at *m/z* 925 $(M+Na)^+$, while the negative-ion FAB-MS showed the quasimolecular ion peak at *m/z* 901 $(M-H)^-$ in addition to fragment ion peaks at *m/z* 755 $(M-C_6H_{11}O_4)^-$, *m/z* 739 $(M-C_6H_{11}O_5)^-$, *m/z* 593 $(M-C_{12}H_{21}O_9)^-$, and *m/z* 431 $(M-C_{18}H_{31}O_{14})^-$. On acid hydrolysis of **4** and **5** with 5% aqueous H_2SO_4–dioxane, D-glucose and L-rhamnose were detected in both cases. Enzymatic hydrolysis of **4** with naringinase gave a new spirostane-type aglycone termed trigonegenin A [25(*S*)-spirost-4-en-3β-ol (**15**)], while 25*R*-stereoisomer called trigonegenin B (**16**)[13] was obtained by the enzymatic hydrolysis of **5**. The ^{1}H-NMR and ^{13}C-NMR (Table 1) spectra of **15** and **16** resembled those of yamogenin (**17**)[6b,14] and diosgenin (**18**),[6b,14] respectively, except for the signals due to the double bond. The 4-en-3β-ol structures of **15**, **16**, **4**, and **5** were confirmed by various NMR experiments,[12] which included a ^{1}H–^{1}H correlation between the 3-proton and the 4-proton in ^{1}H–^{1}H COSY experiments on these compounds. The proton and carbon signals

due to the sugar moieties in the ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[12] of **4** and **5** were similar to those of **1** and **2**, and HMBC experiments on **4** and **5** showed long-range correlations between the following protons and carbons (1″-H and 2′-C; 1′-H and 3-C; 1‴-H and 26-C). The proton signals assignable to the 26-methylene group [δ 3.48, 4.05 (both dd-like)] in the ^{1}H-NMR spectrum of **4** were very similar to those of **1**, while the 26-methylene signals [δ 3.63 (dd, J=6.1, 9.4 Hz), 3.92 (m)] of **5** were very similar to those of **2**. On the basis of the above evidence, the structures of trigoneosides XIIa and XIIb were formulated as 26-*O*-β-D-glucopyranosyl-(25*S*)-furost-4-ene-3β,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside (**4**) and its 25*R*-isomer (**5**).

Trigoneoside XIIIa (**6**) was found to have the molecular formula $C_{57}H_{94}O_{28}$, which was determined from the quasi-molecular ion peaks in the negative-ion [*m/z* 1225 $(M-H)^-$] and positive-ion [*m/z* 1249 $(M+Na)^+$] FAB-MS and by high-resolution MS measurement. Acid hydrolysis of **2** with 5% aqueous H_2SO_4–dioxane liberated D-glucose and L-rhamnose, whereas yamogenin (**17**)[6b,14] and diosgenin (**18**)[6b,14] were obtained by acid hydrolysis of **2** with 2 N HCl–dioxane. The ^{1}H-NMR (pyridine-d_5) spectrum[12] of **6** indicated the presence of the 26-*O*-β-D-glucopyranosyl-(25*S*)-furost-5-ene-3β,22ξ,26-triol part [δ 0.90, 1.06 (both s, 18, 19-H$_3$), 1.03 (d, J=6.7 Hz, 27-H$_3$), 1.31 (d, J=6.7 Hz, 21-H$_3$), 3.49, 4.06 (both dd-like, 26-H$_2$), 3.87 (dd-like, 3-H), 4.78 (d, J=7.9 Hz, 1⁗-H), 4.93 (dd-like, 16-H), 5.30 (br s, 6-H)], three β-D-glucopyranosyl moieties [δ 4.91 (d, J=5.8 Hz, 1′-H), 5.05 (d, J=8.0 Hz, 1‴-H), 5.22 (d, J=6.7 Hz, 1⁗-H)], and an α-L-rhamnopyranosyl moiety [δ 1.74 (d, J=6.1 Hz, 6″-H$_3$), 6.17 (1H, br s, 1″-H)]. The 3,26-bisdesmoside structure of **6** was clarified by a HMBC experiment on **6**, which showed long-range correlations between the 1⁗-proton and 3‴-carbon, between the 1‴-proton and the 4′-carbon, between the 1″-proton and the 2′-carbon, between the 1′-proton and 3-carbon, and between the 1⁗-proton and the 26-carbon. Consequently, the structure of trigoneoside XIIIa was determined to be 26-*O*-β-D-glucopyranosyl-(25*S*)-furost-5-ene-3β,22ξ,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)-β-D-glucopyranosyl(1→4)]-β-D-glucopyranoside (**6**).

Experimental

The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter (l=5 cm); IR spectra, Shimadzu FTIR-8100 spectrometer; ^{1}H-NMR spectra, JNM-LA500 (500 MHz) spectrometer; ^{13}C-NMR spectra, JNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard; MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer and JMS-GCMATE; HPLC, Shimadzu LC-10AS chromatograph.

The following experimental conditions were used for chromatography: normal-phase column chromatography; Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh), reversed-phase column chromatography; Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh): TLC, pre-coated TLC plates with Silica gel 60F$_{254}$ (Merck, 0.25 mm) (normal-phase) and Silica gel RP-18 60F$_{254}$ (Merck, 0.25 mm) (reversed-phase); HPTLC, pre-coated TLC plates with Silica gel RP-18 60WF$_{254S}$ (Merck, 0.25 mm) (reversed-phase). Detection was done by spraying with 1% Ce(SO$_4$)$_2$–10% aqueous H_2SO_4, followed by heating.

Isolation of Trigoneosides Xa (1), Xb (2), XIb (3), XIIa (4), XIIb (5), and XIIIa (6) and Known Compounds (7—12) from the Seeds of *Trigonella foenum-graecum* L. The seeds of *Trigonella foenum-graecum* L. (506 g, cultivated in Egypt) were crushed and extracted three times with MeOH under reflux. Evaporation of the solvent under reduced pressure provided the MeOH extract (96.2 g, 19.0%), and the extract (90 g) was subjected to Diaion HP-20 column chromatography [1 kg (Nippon Rensou Co.), H_2O→MeOH→acetone] to give the H_2O eluate, MeOH eluate (36.6 g, 7.23%) and acetone eluate (24.7 g, 4.94%). Normal-phase silica gel column chromatography [BW-200 (Fuji Silysia Ltd., 810 g), $CHCl_3$–MeOH–H_2O (7 : 3 : 1, lower layer→65 : 35 : 10, lower layer)→MeOH] of the MeOH eluate (27 g) gave seven fractions [fr. 1 (365.4 mg), fr. 2 (600.8 mg), fr. 3 (767.1 mg), fr. 4 (4.2 g), fr. 5 (11.1 g), fr. 6 (4.0 g), fr. 7 (5.3 g)]. Fraction 4 (4.0 g) was separated by reversed-phase silica gel column chromatography [Chromatorex DM1020T (Fuji Silysia, Ltd., 120 g), MeOH–H_2O (50 : 50→60 : 40→70 : 30, v/v)→MeOH] and repeated HPLC [YMC-Pack ODS-AL (250×20 mm i.d., YMC Co., Ltd.), CH_3CN–H_2O (25 : 75, v/v)] to give trigoneosides Xa (**1**, 191 mg, 0.038%), Xb (**2**, 183 mg, 0.031%), XIb (**3**, 13 mg, 0.0026%), XIIa (**4**, 38 mg, 0.0071%), and XIIb (**5**, 30 mg, 0.0059%), trigoneosides Ia (**7**, 48 mg, 0.0095%) and Ib (**8**, 51 mg, 0.010%), and glycoside D (**9**, 115 mg, 0.023%). Fraction 5 (10 g) was separated by reversed-phase silica gel column chromatography [Chromatorex DM1020T (300 g), MeOH–H_2O (50 : 50→60 : 40→70 : 30, v/v)→MeOH] and purified by HPLC [YMC-Pack ODS-AL (250×20 mm i.d.), 1) CH_3CN–H_2O (25 : 75, v/v); 2) CH_3CN–H_2O (30 : 70, v/v)] to give trigonelloside C (**10**, 37 mg, 0.0073%) and compound C (**11**, 104 mg, 0.021%). Fraction 6 (4.0 g) was separated by reversed-phase silica gel column chromatography [Chromatorex DM1020T (300 g), MeOH–H_2O (50 : 50→60 : 40→70 : 30, v/v)→MeOH] and purified by HPLC [YMC-Pack ODS-AL (250×20 mm i.d.), 1) CH_3CN–H_2O (25 : 75, v/v); 2) CH_3CN–H_2O (30 : 70, v/v)] to give trigoneoside XIIIa (**6**, 38 mg, 0.0075%). Fraction 7 (400 mg) was purified by HPLC [YMC-Pack ODS-AL (250×20 mm i.d.), CH_3CN–H_2O (25 : 75, v/v)] to give trigoneoside Va (**12**, 152 mg, 0.030%). The known compounds (**7**—**12**) were identified by comparison of their physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with reported values.[3—6]

Trigoneoside Xa (**1**): A white powder, $[\alpha]_D^{22}$ −49.2° (c=0.6, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{45}H_{76}O_{19}Na$ $(M+Na)^+$: 943.4879. Found: 943.4885. IR (KBr): 3432, 2932, 1072, 1044 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.86, 0.88 (3H each, both s, 18, 19-H$_3$), 1.01 (3H, d, J=6.2 Hz, 27-H$_3$), 1.28 (3H, d, J=6.6 Hz, 21-H$_3$), 1.67 (3H, d, J=5.6 Hz, 6″-H$_3$), 3.47 (1H, dd-like), 4.06 (1H, m) (26-H$_2$), 3.86 (1H, m, 3-H), 4.08 (1H, m, 2-H), 4.76 (1H, d, J=8.2 Hz, 1‴-H), 4.90 (1H, m, 16-H), 5.01 (1H, d, J=7.0 Hz, 1′-H), 6.27 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 919 $(M-H)^-$, 773 $(M-C_6H_{11}O_4)^-$, 757 $(M-C_6H_{11}O_5)^-$, 611 $(M-C_{12}H_{21}O_9)^-$, 449 $(M-C_{18}H_{31}O_{14})^-$. Positive-ion FAB-MS: *m/z* 943 $(M+Na)^+$.

Trigoneoside Xb (**2**): A white powder, $[\alpha]_D^{22}$ −51.5° (c=0.6, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{45}H_{76}O_{19}Na$ $(M+Na)^+$: 943.4879. Found: 943.4885. IR (KBr): 3432, 2932, 1075, 1044 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.86, 0.88 (3H each, both s, 18, 19-H$_3$), 0.98 (3H, d, J=6.7 Hz, 27-H$_3$), 1.30 (3H, d, J=7.0 Hz, 21-H$_3$), 1.68 (3H, d, J=6.4 Hz, 6″-H$_3$), 3.61 (1H, dd, J=6.4, 9.2 Hz), 3.96 (1H, m) (26-H$_2$), 3.86 (1H, m, 3-H), 4.06 (1H, m, 2-H), 4.77 (1H, d, J=7.6 Hz, 1‴-H), 4.91 (1H, ddd-like, 16-H), 5.01 (1H, d, J=7.6 Hz, 1′-H), 6.27 (1H, d, J=1.2 Hz, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 919 $(M-H)^-$, 773 $(M-C_6H_{11}O_4)^-$, 757 $(M-C_6H_{11}O_5)^-$, 611 $(M-C_{12}H_{21}O_9)^-$, 449 $(M-C_{18}H_{31}O_{14})^-$. Positive-ion FAB-MS: *m/z* 943 $(M+Na)^+$.

Trigoneoside XIb (**3**): A white powder, $[\alpha]_D^{23}$ −24.7° (c=0.2, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{44}H_{74}O_{19}Na$ $(M+Na)^+$: 929.4722. Found: 929.4732. IR (KBr): 3432, 2926, 1076, 1044 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.75, 0.87 (3H each, both s, 19, 18-H$_3$), 0.99 (3H, d, J=6.7 Hz, 27-H$_3$), 1.31 (3H, d, J=7.0 Hz, 21-H$_3$), 3.62, 3.93 (1H each, both m, 26-H$_2$), 3.84 (1H, m, 3-H), 3.95 (1H, m, 2-H), 4.79 (1H, d, J=7.6 Hz, 1‴-H), 4.92 (1H, ddd-like, 16-H), 5.01 (1H, d, J=7.6 Hz, 1′-H), 5.10 (1H, d, J=7.3 Hz, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 905 $(M-H)^-$, 773 $(M-C_5H_9O_4)^-$, 611 $(M-C_{11}H_{19}O_9)^-$. Positive-ion FAB-MS: *m/z* 929 $(M+Na)^+$.

Trigoneoside XIIa (**4**): A white powder, $[\alpha]_D^{20}$ −48.8° (c=0.6, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{45}H_{74}O_{18}Na$ $(M+Na)^+$: 925.4773. Found : 925.4776. IR (KBr): 3432, 2932, 1074, 1047 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.91, 1.07 (3H each, both s, 18, 19-H$_3$), 1.01 (3H, d, J=7.2 Hz, 27-H$_3$), 1.29 (3H, d, J=6.7 Hz, 21-H$_3$), 1.67 (3H, d, J=5.8 Hz, 6″-H$_3$), 3.48, 4.05 (1H each, both dd-like, 26-H$_2$), 4.48 (1H, dd-like, 3-H), 4.77 (1H, d, J=7.6 Hz, 1⁗-H), 4.91 (1H, ddd-like, 16-H), 4.99 (1H, d, J=7.6 Hz, 1′-H), 5.81 (1H, br s, 4-H), 6.25 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 901 $(M-H)^-$, 755 $(M-C_6H_{11}O_4)^-$, 739 $(M-C_6H_{11}O_5)^-$, 593 $(M-C_{12}H_{21}O_9)^-$, 431 $(M-C_{18}H_{31}O_{14})^-$. Positive-ion FAB-MS: *m/z* 925 $(M+Na)^+$.

Trigoneoside XIIb (**5**): A white powder, $[\alpha]_D^{22}$ −48.2° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{45}H_{74}O_{18}Na$ $(M+Na)^+$: 925.4773. Found: 925.4776. IR (KBr): 3432, 2932, 1071, 1048 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.92, 1.07 (3H each, both s, 18, 19-H_3), 0.99 (3H, d, J=6.7 Hz, 27-H_3), 1.32 (3H, d, J=6.7 Hz, 21-H_3), 1.68 (3H, d, J=6.1 Hz, 6″-H_3), 3.63 (1H, dd, J=6.1, 9.4 Hz), 3.92 (1H, m) (26-H_2), 4.49 (1H, ddd-like, 3-H), 4.78 (1H, d, J=7.9 Hz, 1‴-H), 4.92 (1H, ddd-like, 16-H), 4.99 (1H, d, J=7.6 Hz, 1′-H), 5.81 (1H, br s, 4-H), 6.23 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: m/z 901 $(M-H)^-$, 755 $(M-C_6H_{11}O_4)^-$, 739 $(M-C_6H_{11}O_5)^-$, 593 $(M-C_{12}H_{21}O_9)^-$, 431 $(M-C_{18}H_{31}O_{14})^-$. Positive-ion FAB-MS: m/z 925 $(M+Na)^+$.

Trigoneoside XIIIa (**6**): A white powder, $[\alpha]_D^{26}$ −31.4° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{57}H_{94}O_{28}Na$ $(M+Na)^+$: 1249.5829. Found: 1249.5817. IR (KBr): 3410, 2934, 1072, 1036 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.90, 1.06 (3H each, both s, 18, 19-H_3), 1.03 (3H, d, J=6.7 Hz, 27-H_3), 1.31 (3H, d, J=6.7 Hz, 21-H_3), 1.74 (3H, d, J=6.1 Hz, 6″-H_3), 3.49, 4.06 (1H each, both dd-like, 26-H_2), 3.87 (1H, dd-like, 3-H), 4.78 (1H, d, J=7.9 Hz, 1⁗-H), 4.91 (1H, d, J=5.9 Hz, 1′-H), 4.93 (1H, dd-like, 16-H), 5.05 (1H, d, J=8.0 Hz, 1‴-H), 5.22 (1H, d, J=6.7 Hz, 1⁗-H), 5.30 (1H, br s, 6-H), 6.17 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: m/z 1225 $(M-H)^-$. Positive-ion FAB-MS: m/z 1249 $(M+Na)^+$.

Acid Hydrolysis of Trigoneosides 1—6 A solution of trigoneosides (**1**—**6**, 5 mg each) in 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v, 2 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the residue was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was transferred to a Sep-Pak C_{18} cartridge with H_2O and MeOH. The H_2O eluate was concentrated and the residue was treated with L-cysteine methyl ester hydrochloride (4 mg) in pyridine (0.5 ml) at 60 °C for 1 h. After reaction, the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) at 60 °C for 1 h. The supernatant was then subjected to GLC analysis to identify the derivatives of D-glucose (i) from **1**—**6**, D-xylose (ii) from **3**, L-rhamnose (iii) from **1, 2, 4**—**6**; GLC conditions: Supeluco STB™-1, 30 m×0.25 mm (i.d.) capillary column, column temperature 230 °C, He flow rate 15 ml/min, t_R: i (24.2 min), ii (15.4 min), iii (13.8 min).

Acid Hydrolysis of 1 Giving Neogitogenin (13) and Gitogenin (14) A solution of **1** (15 mg) in 2 N HCl–dioxane (1 : 1, v/v, 4 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the insoluble portion was removed by filtration. After removal of the solvent *in vacuo* from the filtrate, the crude product (15 mg) was purified by normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (1 : 1)] to give neogitogenin (**13**, 4.0 mg, 54.1%) and gitogenin (**14**, 2.1 mg, 28.4%), which were identified by comparison of their physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with those of authentic samples.[3)]

Acid Hydrolysis of 2 Giving 14 A solution of **2** (15 mg) in 2 N HCl–dioxane (1 : 1, v/v, 4 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the insoluble portion was removed by filtration. After removal of the solvent *in vacuo* from the filtrate, the crude product (15 mg) was purified by normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (1 : 1)] to give gitogenin (**14**, 4.4 mg, 88.7%), which was identified by comparison of the physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with those of an authentic sample.[3)]

Acid Hydrolysis of 3 Giving 14 A solution of **3** (10 mg) in 2 N HCl–dioxane (1 : 1, v/v, 4 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the insoluble portion was removed by filtration. After removal of the solvent *in vacuo* from the filtrate, the crude product (10 mg) was purified by normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (1 : 1)] to give gitogenin (**14**, 1.9 mg, 76.0%), which was identified by comparison of the physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with those of an authentic sample.[3)]

Enzymatic Hydrolysis of Trigoneoside XIIa (4) Giving Trigonegenin A (15) A solution of **4** (10 mg) in 0.2 M acetate buffer (pH 4.0, 4 ml) added with naringinase (Sigma Chemical Co., Ltd., 15 mg) was stirred at 40 °C for 10 h. After EtOH was added to the reaction mixture, the solvent was removed *in vacuo.* The crude product was purified by normal-phase silica gel column chromatography [3 g, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer)] to give trigonegenin A (**15**, 2.1 mg, 46.7%), which was identified by comparison of physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with reported values.[13)]

Trigonegenin A (**15**): A white powder, $[\alpha]_D^{25}$ +16.2° (c=0.1, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{27}H_{42}O_3$ (M^+): 414.3134. Found: 414.3137. IR (KBr): 3474, 1098, 1028, 803 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.79, 1.06 (3H each, both s, 18, 19-H_3), 0.99 (3H, d, J=6.7 Hz, 21-H_3), 1.08 (3H, d, J=7.0 Hz, 27-H_3), 3.29, 3.95 (1H each, both d, J=11.3 Hz, 26-H_2), 4.14 (1H, br s, 3-H), 4.39 (1H, dd-like, 16-H), 5.28 (1H, br s, 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ_C: given in Table 1. EI-MS: m/z 414 (M^+).

Enzymatic Hydrolysis of 5 Giving Trigonegenin B (16) A solution of **5** (10 mg) in 0.2 M acetate buffer (pH 4.0, 4 ml) added with naringinase (Sigma Chemical, Co., Ltd., 15 mg) was stirred at 40 °C for 10 h. After EtOH was added to the reaction mixture, the solvent was removed *in vacuo.* The crude product was purified by normal-phase silica gel column chromatography [3 g, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer)] to give **16** (1.9 mg, 42.2%), which was identified by comparison of physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with reported values.[13)]

Trigonegenin B (**16**): A white powder, $[\alpha]_D^{25}$ −17.6° (c=0.1, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{27}H_{42}O_3$ (M^+): 414.3134. Found: 414.3130. IR (KBr): 3474, 1065, 1053, 808 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.79, 1.06 (3H each, both s, 18, 19-H_3), 0.79 (3H, d, J=4.3 Hz, 27-H_3), 0.96 (3H, d, J=6.8 Hz, 21-H_3), 3.37 (1H, m), 3.47 (1H, dd-like) (26-H_2), 4.14 (1H, br s, 3-H), 4.37 (1H, dd-like, 16-H), 5.28 (1H, br s, 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ_C: given in Table 1. EI-MS: m/z 414 (M^+).

Acid Treatment of 6 Giving Yamogenin (17) and Diosgenin (18) A solution of **6** (15 mg) in 2 N HCl–dioxane (1 : 1, v/v, 4 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the insoluble portion was removed by filtration. After removal of the solvent *in vacuo* from the filtrate, the crude product (15 mg) was purified by normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (1 : 1)] to give **17** (3.0 mg, 58%) and **18** (1.4 mg, 27%), which were identified by comparison of physical data ($[\alpha]_D$, ^{1}H-NMR, ^{13}C-NMR) with reported values.[6b,14)]

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