# New Steroidal Glycosides from the Fruits of *Solanum anguivi*

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Four new steroidal saponins, anguiviosides III (**1**), XI (**2**), XV (**3**), and XVI (**4**), were isolated and characterized from the fruits of *Solanum anguivi*. Their structures were elucidated on the basis of spectroscopic analysis. The occurrence of the cholestane glycosides **3** and **4** is considered from a biogenetic point of view.

We have examined so far more than 40 *Solanum* species and obtained a large number of steroidal glycosides possessing cytotoxicity,[1] antifeedant,[2] and anti HSV-1[3] activities. Some of these compounds act as key intermediates in the biosynthesis of spirosolane and solanidane.[4] In a continuing search for bioactive substances among the solanaceous species, we have isolated four new glycosides, anguiviosides III, XI, XV, and XVI (**1**−**4**), from the fruits of *Solanum anguivi* Lam. This paper describes the structural characterization of these new steroidal glycosides (**1**−**4**).

Anguivioside III (**1**), obtained as a white powder, $[\alpha]_D$ −67.4° (MeOH), showed a quasimolecular ion peak $[M + Na + H]^+$ at *m/z* 910 in the positive FABMS, suggesting its molecular formula to be $C_{44}H_{70}O_{18}$ when combined with the results of elemental analysis. Acid hydrolysis of **1** gave D-glucose, D-xylose, and L-rhamnose, whose absolute configurations were determined by GLC of their respective trimethylsilyl L-cysteine derivative.[5] The aglycon of **1** could not be obtained owing to its decomposition during acid hydrolysis. The $^1$H NMR spectrum of **1** showed two angular methyl groups at $\delta$ 1.01 (6H, s, $H_3$-18 and -19) and two secondary methyl groups at $\delta$ 1.17 (3H, d, $J$ = 6.1 Hz, $H_3$-27) and 1.27 (3H, d, $J$ = 6.7 Hz, $H_3$-21), being characteristic for a typical steroidal glycoside,[6] and three anomeric proton signals at $\delta$ 4.97 (2H, d, $J$ = 7.3 Hz, H-1 of $\beta$-D-xylopyranosyl and $\beta$-D-glucopyranosyl) and $\delta$ 6.30 (1H, br s, α-L-rhamnopyranosyl H-1). The 27 signals that originated from the aglycon in the $^{13}$C NMR spectrum represented one hemiacetal ($\delta$ 96.1), one ketal ($\delta$ 113.5), three oxygenated methines ($\delta$ 67.4, 77.9, and 81.7), a trisubstituted double bond ($\delta$ 121.9 and 140.8), eight methylenes, six methines, four methyls, and two quaternary carbons. The HMBC spectrum showed correlations between $H_3$-27 and C-26 ($\delta$ 96.1), $H_3$-21 and C-22 ($\delta$ 113.5), H-23 (overlapped around at $\delta$ 3.98) and C-22, and $H_3$-19 and C-5 ($\delta$ 140.8), suggesting the aglycon of **1** to be a 3,23,26-trihydroxyspirost-5-ene derivative.[7] The H-26 signal appeared as a doublet of $J$ = 7.9 Hz at $\delta$ 5.20, indicating *trans*-diaxial coupling with H-25. Moreover, in the NOESY spectrum, correlations were observed between H-20 ($\delta$ 3.01) and H-23 ($\delta$ 3.98), and H-23 and H-25 ($\delta$ 2.00), indicating C-22 and -25 to be both in the *R* configuration, while, in the sugar region, HMBC was observed between the rhamnosyl H-1 and the glucosyl C-2 ($\delta$ 77.4), the xylosyl H-1 and the glucosyl C-3 ($\delta$ 88.2), and the glucosyl H-1 and the C-3 ($\delta$ 77.9) of the aglycon moiety. Consequently, the structure of **1** was characterized as 3-*O*-[$\beta$-D-xylopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-$\beta$-D-glucopyranosyl (22*R*,23*S*,25*R*,26*R*)-3$\beta$,23,26-trihydroxyspirost-5-ene.

Anguivioside XI (**2**) was obtained as a white powder showing $[\alpha]_D$ −61.4° (MeOH) and a quasimolecular ion peak $[M + Na + H]^+$ at *m/z* 1072 in the positive FABMS, which suggested a molecular formula of $C_{50}H_{80}O_{23}$. This value was supported by the results of elemental analysis. Compound **2** gave a pink coloration with Ehrlich reagent, indicating that it is a furostanol glycoside.[8] The $^{13}$C NMR signals included resonances for a terminal [$\beta$-D-xylopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-$\beta$-D-glucopyranosyl moiety, identical to that of **1**, and one additional terminal $\beta$-D-glucopyranosyl moiety as a sugar residue. The remaining 27 signals in the aglycon part were composed of four methyl groups ($\delta$ 16.3, 16.5, 16.7, 19.4), eight methylenes, six methines, two quaternary carbons, one trisubstituted double bond ($\delta$ 140.7 and 121.9), three oxygenated methine carbons ($\delta$ 77.7, 81.4, 85.0), one hemiketal carbon ($\delta$ 109.1), and one hemiacetal carbon ($\delta$ 107.2). The HMBC revealed the connectivities of the triglycosyl [inner glucosyl H-1 at $\delta$ 4.98 (1H, d, $J$ = 7.3 Hz)] to C-3 at $\delta$ 77.7, and the glucosyl H-1 ($\delta$ 5.33, d, $J$ = 8.6 Hz) to C-26, and the locations of the respective functional groups: the double bond at C-5, the hemiketal carbon at C-22, the hemiacetal carbon at C-26, and the methine at C-23 adjacent to the epoxide ring between C-23 and C-26. Moreover, NOESY correlations were observed between H-23 at $\delta$ 4.58 (overlapped) and $H_3$-27, and H-26 at $\delta$ 5.50 (s) and $H_3$-27 at $\delta$ 0.84 (3H, d, $J$ = 7.3 Hz); therefore, assuming the configuration at C-25 was the same as that of **1**, the structure of **2** can be represented as 3-*O*-[$\beta$-D-xylopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-$\beta$-D-glucopyranosyl (22*S*,23*S*,25*R*,26*S*)-3$\beta$,22α,26-trihydroxyfurost-5-en-23,26-epoxide 26-*O*-$\beta$-D-glucopyranoside.

Anguivioside XV (**3**) was obtained as a white powder, showing $[\alpha]_D$ −88.1° (MeOH) and a quasimolecular ion peak $[M + Na + H]^+$ at *m/z* 1070 in the positive FABMS, which suggested its molecular formula to be $C_{51}H_{82}O_{22}$, as supported by elemental analysis. Absorptions at $\nu_{max}$ 1742 and 1711 cm$^{-1}$ in the IR spectrum suggested the presence of carbonyl groups. Assignments of the $^{13}$C NMR signals and the HMBC spectrum indicated the presence of a [α-L-rhamnopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-$\beta$-D-glucopyranosyl unit, a $\beta$-chacotriosyl moiety[9] at the hydroxy group at C-3, and a $\beta$-D-glucopyranosyl moiety at the hydroxy at C-26. The $^{13}$C NMR signals due to the aglycon part were superimposable on those of 3$\beta$,26-dihydroxycholest-5-ene 16,22-dione, kryptogenin,[10] except for those

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of C-26 and C-3. Therefore, the structure of **3** was determined as 3-*O*-$\beta$-chacotriosyl kryptogenin 26-*O*-$\beta$-D-glucopyranoside.

Anguivioside XVI (**4**) was obtained as a white powder showing $[\alpha]_D$ −112.4° (MeOH) and a quasimolecular ion peak $[M + Na + H]^+$ at *m*/*z* 1084 in the positive FABMS, which when taken in combination with the elemental analysis data suggested its molecular formula to be $C_{51}H_{80}O_{23}$. The $^1$H NMR spectrum displayed signals due to two tertiary methyl groups at $\delta$ 0.85 ($H_3$-18) and 1.06 ($H_3$-19), two secondary methyl groups at $\delta$ 0.81 ($\delta$, $J$ = 6.7 Hz, $H_3$-27) and 1.26 ($\delta$, $J$ = 6.7 Hz, $H_3$-21), and two methyl pentosyl $H_3$-6 signals at $\delta$ 1.64 ($\delta$, $J$ = 6.2 Hz) and 1.78 ($\delta$, $J$ = 6.7 Hz). The $^{13}$C NMR signals of **4** resembled those of **3** in respect to the presence of two carbonyl groups at $\delta$ 214.8 and 217.8, a terminal $\beta$-D-glucopyranosyl moiety, and a $\beta$-chacotriosyl moiety. The HMBC spectrum revealed the occurrence of an epoxide ring between C-23 ($\delta_C$ 84.9, $\delta_H$ 5.10, dd, $J$ = 2.5, 7.0 Hz) and C-26, and an acetal carbon at $\delta_C$ 107.3 ($\delta_H$ 5.67, s). Furthermore, in the NOESY spectrum, correlations were observed between H-23 and $H_3$-27, and H-26 and $H_3$-27. Because the absolute configuration at C-25 was regarded as the same as those of **1**−**3**, and the singlet signal due to H-26 indicated the dihedral angle between H-25 and H-26 to be 90°, the configurations at C-23, 25, 26 were assigned as *S*, *R*, *S*, respectively. Consequently, the structure of **4** was established as 3-*O*-$\beta$-chacotriosyl (23*S*,25*R*,26*S*)-3$\beta$,26-dihydroxycholest-5-en-23,26-epoxide 26-*O*-$\beta$-D-glucopyranoside.

Anguiviosides III (**1**) and XI (**2**) are hydroxylated at C-23 and C-26 on the spirostanol and furostanol skeletons, respectively. Anguiviosides XV (**3**) and XVI (**4**) are based on a 16,22-dicarbonyl aglycon, with **4** hydroxylated at C-23 and C-26 followed by ring closure. The biogenetic pathway of 16,22-dicarbonyl compounds such as **3** and **4** might be considered via a 17$\alpha$-hydroxy spirostanol such as pennogenin,[11] or via a 3$\beta$,16$\beta$,22,26-tetrahydroxycholesterol glycoside such as anguivioside A.[12] Compounds **3** and **4** steroidal glycosides are worthy of consideration in respect of the proposal of a novel biogenetic pathway leading to the kryptogenin-type glycosides.

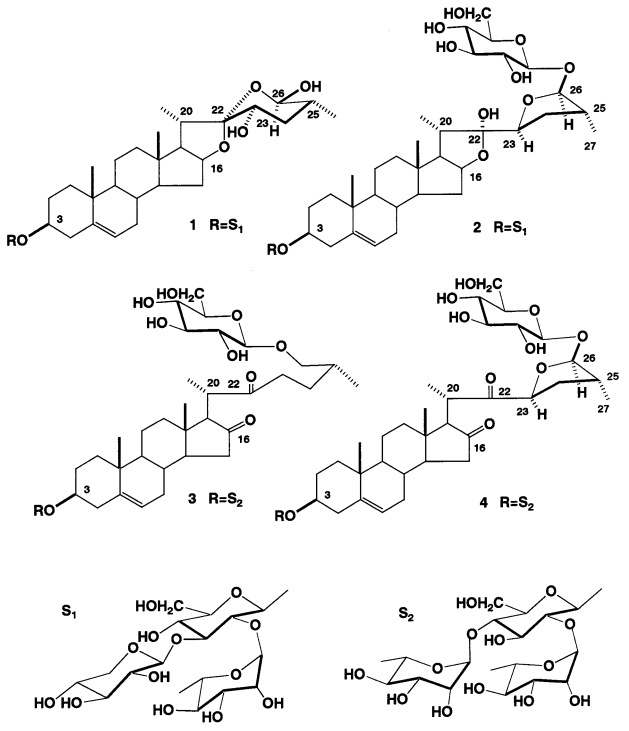


**Table 1.** $^{13}$C NMR Data of **1**−**4** (Pyridine-$d_5$)

| $^{13}$C | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| C-1 | 37.5 | 37.1 | 37.2 | 37.2 |
| 2 | 30.1 | 30.1 | 30.1 | 30.1 |
| 3 | 77.9 | 77.7 | 77.8 | 77.8 |
| 4 | 38.7 | 38.7 | 38.7 | 38.8 |
| 5 | 140.8 | 140.7 | 140.9 | 141.0 |
| 6 | 121.9 | 121.9 | 121.5 | 121.5 |
| 7 | 32.3 | 32.4 | 32.0 | 32.0 |
| 8 | 31.4 | 31.8 | 31.0 | 31.0 |
| 9 | 50.3 | 50.3 | 50.0 | 50.0 |
| 10 | 37.1 | 37.1 | 37.1 | 37.1 |
| 11 | 21.1 | 21.0 | 20.7 | 20.7 |
| 12 | 40.2 | 39.7 | 40.2 | 39.0 |
| 13 | 41.0 | 40.9 | 41.7 | 41.9 |
| 14 | 56.6 | 56.7 | 51.1 | 51.1 |
| 15 | 32.1 | 32.3 | 39.0 | 37.5 |
| 16 | 81.7 | 81.4 | 217.8 | 217.8 |
| 17 | 62.6 | 64.6 | 66.4 | 66.4 |
| 18 | 16.6 | 16.3 | 12.9 | 13.1 |
| 19 | 19.4 | 19.4 | 19.4 | 19.4 |
| 20 | 41.6 | 39.2 | 43.7 | 39.3 |
| 21 | 14.8 | 16.5 | 15.6 | 15.6 |
| 22 | 113.5 | 109.1 | 213.0 | 214.8 |
| 23 | 67.4 | 85.0 | 37.4 | 84.9 |
| 24 | 30.1 | 32.1 | 27.8 | 35.0 |
| 25 | 36.2 | 40.2 | 33.5 | 39.9 |
| 26 | 96.1 | 107.2 | 75.1 | 107.3 |
| 27 | 17.4 | 16.7 | 17.5 | 15.9 |
| 3-*O*-glc | | | | |
| 1 | 99.9 | 99.9 | 100.3 | 100.3 |
| 2 | 77.4 | 78.3 | 78.5 | 78.7 |
| 3 | 88.2 | 88.2 | 77.0 | 77.0 |
| 4 | 69.5 | 69.6 | 78.0 | 78.4 |
| 5 | 77.7 | 77.4 | 77.8 | 78.0 |
| 6 | 62.3 | 62.3 | 61.3 | 61.3 |
| -glc(2→1)-rha | | | | |
| 1 | 102.4 | 102.4 | 102.1 | 102.1 |
| 2 | 72.4 | 72.4 | 72.5 | 72.5 |
| 3 | 72.8 | 72.8 | 72.8 | 72.9 |
| 4 | 74.0 | 74.1 | 73.9 | 73.9 |
| 5 | 69.6 | 69.5 | 69.5 | 69.5 |
| 6 | 18.7 | 18.7 | 18.5 | 18.5 |
| -glc(4→1)-rha | | | | |
| 1 | | | 102.9 | 103.0 |
| 2 | | | 72.6 | 72.6 |
| 3 | | | 72.8 | 72.8 |
| 4 | | | 73.9 | 74.2 |
| 5 | | | 70.4 | 70.5 |
| 6 | | | 18.7 | 18.7 |
| xyl | | | | |
| 1 | 105.4 | 105.4 | | |
| 2 | 74.6 | 74.6 | | |
| 3 | 78.3 | 78.7 | | |
| 4 | 70.6 | 70.7 | | |
| 5 | 67.2 | 67.2 | | |
| 26-*O*-glc | | | | |
| 1 | | | 104.9 | 100.3 |
| 2 | | | 75.3 | 75.2 |
| 3 | | | 78.0 | 78.1 |
| 4 | | | 71.8 | 71.5 |
| 5 | | | 78.7 | 78.9 |
| 6 | | | 62.9 | 62.5 |

## Experimental Section

**General Experimental Procedures.** Optical rotations were measured with a JASCO DIP-1000 KUY polarimeter ($l$ = 0.5). NMR spectra were measured in pyridine-$d_5$ on a JEOL $\alpha$-500 spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). FABMS was obtained with a glycerol matrix in the positive ion mode using a JEOL JMS-DX-303HF spectrometer. GLC was performed on an HP5890A gas chromatograph with a flame ionization detector (FID). Column chromatography was carried out with silica gel 60 (Art. 7734 and Art. 9385, Merck), Sephadex LH-20 (Pharmacia Fine Chemicals), Diaion HP-20P (Mitsubishi Chemical Indus-

tries Co., Ltd.), and Chromatorex ODS (Fuji Silysia Chemical Co., Ltd.), and TLC was performed on a precoated silica gel $60F_{254}$ (Merck) and RP-18 $F_{254S}$ (Merck). HPLC separations were run on a TOSOH dual pump CCPS instrument with a TOSOH RI-8010 detector. For HPLC column chromatography, COSMOSIL $5C_{18}$ AR-II (4.6 × 250 mm) for analytical and preparative applications was used.

**Plant Material.** The seeds of the title plant were provided by Dr. Tatemi Yoshida (National Research Institute of Vegetables, Ornamental Plants and Tea, Ministry of Agriculture, Forestry, and Fisheries, Ano, Mie, Japan), cultivated at the Botanical Garden of Kumamoto University, and harvested in September, 2000. A voucher specimen (number KUP-15 Sep 00-5) is deposited in the Herbarium of the Botanical Garden of Kumamoto University, Japan.

**Extraction and Isolation.** The fruits (399 g) were extracted with hot MeOH, and the solvent removal gave a dried extract (33.33 g), which was successively chromatographed on Diaion HP-20 (water and MeOH gradiently increasing MeOH), Sephadex LH-20 (MeOH), Chromatorex ODS (60%, 70%, and 80% MeOH), silica gel ($CHCl_3$−MeOH−water 8:2:0.2 and 7:3:0.5), and HPLC (70% MeOH, COSMOSIL $5C_{18}$ AR-II) to provide anguivioside III (**1**, 53 mg), anguivioside XI (**2**, 32 mg), anguivioside XV (**3**, 11 mg), and anguivioside XVI (**4**, 12 mg).

**Anguivioside III (1).** White powder, $[\alpha]^{26}_D$ −67.4° (*c* 0.6, MeOH); $^1$H NMR (pyridine-$d_5$) $\delta$ 1.01 (3H, s, $H_3$-18), 1.01 (3H, s, $H_3$-19), 1.17 (3H, d, $J$ = 6.1 Hz, $H_3$-27), 1.27 (3H, d, $J$ = 6.7 Hz, $H_3$-21), 1.75 (3H, d, $J$ = 6.1 Hz, rha $H_3$-6), 3.98 (overlapped, H-23), 4.97 (each 1H, d, $J$ = 7.3 Hz, glc H-1 and xyl H-1), 5.20 (1H, d, $J$ = 7.9 Hz, H-26), 5.29 (1H, m, H-6), 6.31 (1H, s, rha H-1); $^{13}$C NMR (pyridine-$d_5$), see Table 1; positive FABMS *m/z*: 910 $[M + Na + H]^+$; *anal*. C 59.53%, H 7.96%, calcd for $C_{44}H_{70}O_{18}$, C 59.58%, H 7.95%.

**Anguivioside XI (2).** White powder, $[\alpha]^{26}_D$ −61.4° (*c* 0.7, MeOH); $^1$H NMR (pyridine-$d_5$) $\delta$ 0.84 (3H, d, $J$ = 7.3 Hz, $H_3$-27), 0.92 (3H, s, $H_3$-18), 1.04 (3H, s, $H_3$-18), 1.27 (3H, d, $J$ = 6.7 Hz, $H_3$-21), 1.75 (3H, d, $J$ = 6.1 Hz, rha $H_3$-6), 4.58 (overlapped, H-23), 4.98 (each 1H, d, $J$ = 6.7 Hz, 3-*O*-glc H-1 and xyl H-1), 5.33 (1H, d, $J$ = 8.6 Hz, 26-*O*-glc H-1), 5.50 (1H, s, H-26), 6.30 (1H, s, rha H-1); $^{13}$C NMR (pyridine-$d_5$), see Table 1; positive FABMS *m/z* 1072 $[M + Na + H]^+$; *anal*. C 57.29%, H 7.66, calcd for $C_{50}H_{80}O_{23}$, C 57.24%, H 7.69%.

**Anguivioside XV (3).** White powder, $[\alpha]^{26}_D$ −88.1° (*c* 0.6, MeOH); $^1$H NMR (pyridine-$d_5$) $\delta$ 0.69 (3H, s, $H_3$-18), 1.02 (3H, d, $J$ = 6.7 Hz, $H_3$-27), 1.05 (3H, d, $J$ = 6.7 Hz, $H_3$-21), 1.07 (3H, s, $H_3$-19), 1.64 (3H, d, $J$ = 6.7 Hz, rha $H_3$-6), 1.78 (3H, d, $J$ = 6.1 Hz, rha $H_3$-6), 4.98 (overlapped with DOH, 3-*O*- and 26-*O*-glc H-1), 5.31 (1H, m, H-6), 6.86 (1H, s, rha H-1), 6.41 (1H, s, rha H-1); $^{13}$C NMR (pyridine-$d_5$), see Table 1; positive FABMS *m/z* 1070 $[M + Na + H]^+$; *anal*. C 58.44%, H 7.82%, calcd for $C_{51}H_{82}O_{22}$, C 58.49%, H 7.89%.

**Anguivioside XVI (4).** White powder, $[\alpha]^{26}_D$ −112.4° (*c* 0.7, MeOH); $^1$H NMR (pyridine-$d_5$) $\delta$ 0.81 (3H, d, $J$ = 6.7 Hz, $H_3$-27), 0.85 (3H, s, $H_3$-18), 1.06 (3H, s, $H_3$-19), 1.26 (3H, d, $J$ = 6.7 Hz, $H_3$-21), 1.64 (3H, d, $J$ = 6.2 Hz, rha $H_3$-6), 1.78 (3H, d, $J$ = 6.7 Hz, rha $H_3$-6), 5.10 (1H, dd, $J$ = 2.5, 7.0 Hz, H-23), 4.97 (1H, d, $J$ = 6.7 Hz, 3-*O*-glc H-1), 5.31 (1H, d, $J$ = 7.9 Hz, 26-*O*-glc H-1), 5.67 (1H, s, H-26), 5.87 (1H, rha H-1), 6.41 (1H, s, rha H-1); $^{13}$C NMR (pyridine-$d_5$), see Table 1; positive FABMS *m/z* 1084 $[M + Na + H]^+$; *anal*. C 57.69%, H 7.57%, calcd for $C_{51}H_{80}O_{23}$, C 57.72%, H 7.60%.

**Analysis of Sugar Components of 1−4.** Compounds **1**−**4** were hydrolyzed with 2 mol/L HCl in $H_2O$ at 80 °C for 3 h. The reaction mixture was neutralized with 2 mol/L NaOH in $H_2O$ and extracted with $CHCl_3$. The aqueous layer was concentrated to dryness in vacuo to give a residue which was dissolved in dry pyridine; L-cysteine methyl ester hydrochloride was then added to the solution. The reaction mixture was heated at 60 °C for 2 h and concentrated to dryness using $N_2$. To the residue was added trimethylsilylimidazole, and the mixture was heated at 60 °C for 1 h. The reaction mixture was concentrated to dryness, the residue was extracted with a mixture of hexane and $H_2O$, and the organic layer was analyzed by gas liquid chromatography (GLC); column: OV-17 (0.32 mm × 30 m), detector: FID, column temp.: 230 °C, injector temp.: 270 °C, carrier gas: He (2.2 kg/cm$^2$). Each peak was observed at $t_R$ (min); 17′16″ (D-glc), 11′71″ (L-rha), 9′82″ (D-xyl). The standard monosaccharides were subjected to the same reaction and GLC analysis under the same condition.

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