A New Spirostanol Glycoside from Fruits of Solanum indicum L.

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A new characteristic steroidal glycoside of the 23S,26R-hydroxylated spirostanol-type named indioside F was isolated from the fruit of Solanum indicum, along with indioside A and protodioscin. On the basis of spectroscopic analysis, the structure of indioside F was found to be 3-O-α-ribo-hexopyranosyl-(1→2)-(α-L-rhamnopyranosyl-(1→4))-β-D-glucopyranosyl (β-chacotriosyl) (22R,23S,25R,26R)-spirost-5-ene-3β,23,26-triol.

Key words Solanum indicum; fruit; steroidal glycoside; spirostanol

Solanum indicum L. belongs to the Solanaceae family. It has been used in Chinese folk medicine as antiinflammatory and wound-healing agents, as an analgesic, and for the treatment of rhinitis, cough, and breast cancer.1) In Thailand, fruits of S. indicum and S. torvum are available in the markets; these are used as vegetables and as essential ingredients in anticarcinogens. Previously, Nohara et al. isolated new steroidal glycosides from the fruits (indiosides A and B) and roots (indiosides C, D, and E) of S. indicum.2) Indioside D was isolated from the fruit of the tobacco hornworm.3) In our recent study on the constituents of the fruits cultivated in the botanical garden of Sojo University, we successfully achieved the isolation and structural characterization of a new steroidal glycoside, indioside F, along with indioside A and protodioscin.

The methanolic extract obtained from the fruits was subjected to Diaion HP-20, silica gel, and octadecyl silica (ODS) chromatographies to afford three compounds 1—3. Compounds 2 and 3 were well-known steroidal glycosides and were identified as indioside A1—3) and protodioscin,4,5) respectively. This paper deals with the structure elucidation of the new compound 1.

Compound 1, which was obtained as an amorphous powder [α]D = −25.8° (MeOH), exhibited a quasi-molecular ion peak at m/z 924 due to [M + Na]+ in the positive FAB-MS. The molecular formula was estimated as C45H72O18. The 1H-NMR (pyridine-d5) spectrum of 1 indicated two tertiary methyl groups at δ 0.94 (3H, d, J=6.9 Hz, H3-18) and 0.95 (3H, s, H3-17) and two secondary methyl groups at δ 1.26 (3H, s, H3-19) and δ 1.29 (3H, s, H3-20). The 13C-NMR (pyridine-d5) spectrum showed 27 signals that originated from the sugar moiety and two terminal spirostanol moieties. The 1H-NMR (pyridine-d5) and the 13C-NMR (pyridine-d5) spectra revealed that the sapogenol moiety was a 3α,23,26-trihydroxy-3β-spirost-5-ene derivative.

The heteronuclear multiple bond correlation (HMBC) spectrum (Fig. 1) showed correlations from H3-23 (3H, d, J=5.7 Hz) at δ 1.09 to C-26 at δ 96.0, a ketal (δ 113.4), three oxygenated methines (δ 67.0, 77.7, 81.6), a tri-substituted double bond (δ 121.6, 140.6), eight methylenes (δ 37.3, 30.0, 40.9, 32.2, 19.3, 38.2, 31.6, 37.3), six methines (δ 31.4, 50.1, 56.5, 62.4, 36.1, 38.8), four methyls (δ 16.4, 19.2, 14.7, 17.2), and two quaternary carbons (δ 37.0, 40.8). In addition, the 13C-NMR spectrum indicated 18 carbon signals that originated from the sugar moiety and two terminal α-L-rhamnopyranosyl moieties; the remaining carbon signals were attributed to the 2,4-di-substituted β-D-glucopyranosyl moiety. The heteronuclear multiple bond correlation (HMBC) spectrum (Fig. 1) showed correlations from H1-27 (3H, d, J=5.7 Hz) at δ 1.09 to C-26 at δ 96.0, from H1-21 (3H, d, J=6.8 Hz) at δ 1.26 to C-22 at δ 113.4, and from H-23 (1H, dd, J=3.0, 9.2 Hz) at δ 3.96 to C-22, suggesting that the aglycone of 1 was a 3α,23,26-trihydroxy-5-ene derivative. The signal due to H-26 appeared as a doublet at δ 5.10 (J=8.0 Hz), indicating trans-diaxial coupling between H-26 and H-25. Moreover, in the nuclear Overhauser effect spectroscopy (NOESY) spectrum (Fig. 1), correlations were observed between H-20 (δ 3.00) and H-23 (δ 3.96), and between H-23 and H-25 (δ 2.03), indicating that C-22 and C-25 were both in the R configuration, while in the sugar region, HMBC was observed from the rhamnosyl H-1 at δ...
was characterized as 3-
aqueous fraction was subjected to Diaion HP-20 eluting with H2O and
jected to ODS eluted with 60% MeOH to give compound
fractions (1—6). Fr. 6 was compound
given on a
cone moiety at
glucosyl H-1 (1H, d,
glycerol matrix in the positive ion mode using a JEOL JMS-DX300 and a
1020 (Fig. 1. Structure of Compound

5.76 to the glucosyl C-2 at δ 78.0, from the 2nd rhamnol
H-1 at δ 6.29 to the glucosyl C-4 at δ 77.7, and from the

Experimental

General Procedure Optical rotations were measured with a JASCO P-
1020 (i=0.5) automatic digital polarimeter. FAB-MS were obtained with a
glycerol matrix in the positive ion mode using a JEOL JMS-DX300 and a
JMS-DX 303 HF spectrometer. The 1H and 13C-NMR spectra were mea-
ured in pyridine-d5 with JEOL α-500 spectrometer, and chemical shifts
are given on a δ (ppm) scale with tetramethylsilane (TMS) as the internal
standard. Column chromatographies were carried out on a Diaion HP-20 (Mi-
tsubishi Chemical Ind.). silica gel 60 (230—400 mesh, Merck), and ODS
(Wako Pure Chemical Industries, Ltd.). TLC was performed on silica gel
plates (Kieselgel 60 F254, Merck) and RP C18 silica gel plates (Merck). The
spots on TLC were visualized by UV light (254/366 nm) and sprayed with
a solution of compound (1) (1.0 mg) in 2 mL HCl/diox-
ane (1:1, 2 ml) was heated at 100 °C for 1 h. The reaction mixture was dia-
tes with H2O and evaporated to remove dioxane. The solution was neutral-
ized with Amberlite MB-3 and passed through a SEP-PAC C18 cartridge to
give a sugar fraction. The sugar fraction was concentrated to dryness in
vacuo to give a residue, which was dissolved in CH3CN/H2O (3:1, 250 μl).

Sugar Analysis A solution of compound (1) (1.0 mg) in 2 mL HCl/diox-
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