Journal of Pharmacognosy and Phytochemistry

Available online at www.phytojournal.com

J P P Journal of Pharmacognosy and Phytochemistry

E-ISSN: 2278-4136
P-ISSN: 2349-8234
JPP 2015; 3(6): 252-255
Received: 03-02-2015
Accepted: 01-03-2015

Hari Prasad Devkota
(A) Program for Leading Graduate School, HIGO Program, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862-0973, Japan.
(B) Graduate School of Pharmaceutical Sciences, Kumamoto University, Kumamoto, Japan.

Khem Raj Joshi
(A) Program for Leading Graduate School, HIGO Program, kumamoto University, 5-1 Oe-honmachi, Kumamoto 862-0973, Japan.
(B) Graduate School of Pharmaceutical Sciences, Kumamoto University, Kumamoto, Japan.

Tomomi Ozasa
School of Pharmacy, Kumamoto University, Kumamoto, Japan.

Soko Fukunaga
School of Pharmacy, Kumamoto University, Kumamoto, Japan.

Naotoshi Yoshida
School of Pharmaceutical Sciences, Health Sciences University of Hokkaido, Hokkaido, Japan.

Shoji Yahara
Graduate School of Pharmaceutical Sciences, Kumamoto University, Kumamoto, Japan School of Pharmacy, Kumamoto University, Kumamoto, Japan.

Correspondence:
Hari Prasad Devkota,
Program for Leading Graduate School, HIGO Program, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862-0973, Japan.

Steroidal glycosides from the fruits, aerial parts and tubers of potato (*Solanum tuberosum*)

Hari Prasad Devkota, Khem Raj Joshi, Tomomi Ozasa, Soko Fukunaga, Naotoshi Yoshida and Shoji Yahara

Abstract
α-Chaconine (**1**), *α*-solanine (**2**) and chlorogenic acid (**3**) were isolated from the fresh unripe fruits of potato (*Solanum tuberosum*). Similarly, *α*-chaconine (**1**), α-solanine (**2**), aculeatiside A (**4**) and B (**5**) were isolated from aerial parts and *α*-chaconine (**1**), *α*-solanine (**2**), and protodioscin (**6**) were isolated from the tubers. The structures of these compounds were elucidated on the basis of their physical and spectroscopic data and comparison with reported literature values.

Keywords: Potato, *Solanum tuberosum*, fruits, *α*-chaconine, α-solanine, steroidal glycosides

1. Introduction
Potato (*Solanum tuberosum* L.) is one of the most widely consumed vegetables belonging to the family Solanaceae. Many solanaceous plants are reported to contain steroidal glycoalkaloids. *α*-Chaconine (**1**) and *α*-solanine (**2**) are the main steroidal glycoalkaloids in potato [1, 2]. Although toxic in nature, these glycoalkaloids are receiving more attention in recent years due to their beneficial effects such as anticancer, anti-inflammatory, anti-allergic, anti-bacterial and anti-fungal activities etc. [2, 3]. Extensive studies on the variation of glycoalkaloids in different plant parts of potato suggested that the highest content is found in flowers followed by leaves, stems and tubers [1, 2]. Zhang *et al*. [3] recently reported the steroidal glycosides, including *α*-solanine (**2**) from the aerial parts. However, there has been no report on the isolation of steroidal glycosides and other compounds from fresh unripe fruits. Thus, in this paper, we report the isolation and identification of two steroidal alkaloid glycosides (**1** and **2**) and chlorogenic acid (**3**) from the fruits along with steroidal glycosides from aerial parts and tubers (Fig. 1).

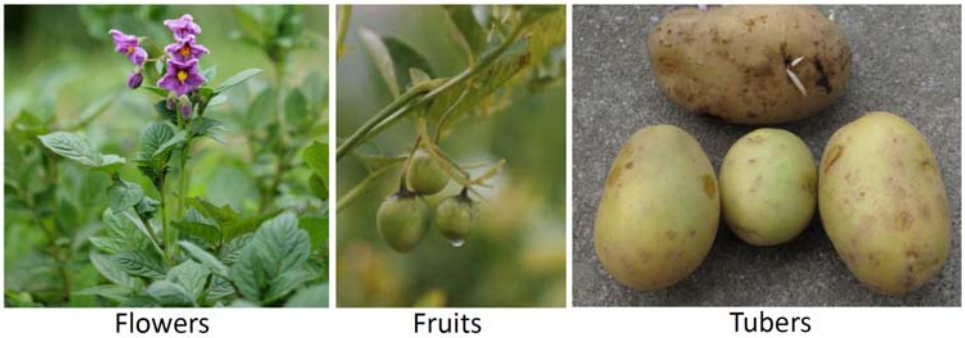

Fig 1: Photographs of flowers, fruits and tubers of Potato.

2. Materials and Methods
2.1. General Experimental Procedures
Optical rotations were measured with a JASCO DIP-1000KUY polarimeter. ^{1}H-, ^{13}C- spectra were measured on a JEOL *α*–500 spectrometer (^{1}H-NMR: 500MHz and ^{13}C-NMR: 125 MHz) using TMS as internal standard. Column chromatography was carried out with MCI gel CHP20P (75 ~ 150 *μ*m, Mitsubishi Chemical Industries Co., Ltd.), Sephadex LH-20 (Amersham Pharmacia Biotech) and Chromatorex NH (Fuji Silysia Chemical Co., Ltd.). TLC was performed on a precoated silica gel 60 F254 (0.2 mm, aluminum sheet, Merck).

2.2. Plant materials

The fresh unripe fruits of potato (*Solanum tuberosum* L, cv. Kitaakari) were collected from Hokkaido, Japan. Fresh aerial parts and tubers were collected from the potato (*Solanum tuberosum* L, cv. May Queen) cultivated at Medicinal Plant Garden, Kumamoto University, Kumamoto, Japan.

2.3. Extraction and isolation

Fresh unripe fruits (485 g) were extracted twice with MeOH (2.5 L). After removal of the solvent under reduced pressure, the concentrated extract (17.0 g) was subjected to chromatography on MCI gel CHP20P column eluting with water, 40% MeOH, 70% MeOH, 100% MeOH and 1% ammonia in MeOH to give 8 fractions. Among those, fraction 4 (232 mg) was subjected to Sephadex LH20 column eluting with MeOH to obtain chlorogenic acid (3, 20 mg). Fraction 8 (358 mg) was subjected to Chromatorex NH (Fuji Silysia Chemical Ltd.) column eluting with $CHCl_3$: MeOH: H2O (7:3:0:5) to obtain α-solanine (**2**) (17 mg) and α-chaconine (**1**) (30 mg).

Dried aerial parts (1.5 kg) were extracted with MeOH and the extract was separated in the similar ways to obtain α-solanine (**2**) (39 mg), α-chaconine (**1**) (21 mg), aculeatiside A (**4**) (48 mg) and aculeatiside B (**5**) (19 mg).

Fresh whole tubers (9.75 kg) were also extracted with MeOH and the extract was separated in the similar ways to obtain α-solanine (**2**) (70 mg), α-chaconine (**1**) (122 mg) and protodioscin (**6**) (8 mg).

2.4. α-Chaconine (1)

A white amorphous powder; $[\alpha]_D^{30}$ -57° (*c* 0.53, pyridine), ^{1}H-NMR (pyridine d_5) δ: 0.83 (3H, d, *J* =5.9 Hz), 0.98 (3H, d, *J* =5.5 Hz), 1.02 (3H, s), 1.17 (3H, s), 1.61 (3H, d, *J* =5.9 Hz), 1.75 (3H, d, *J* =5.9 Hz), 2.81 (2H, m, *J* =5.9 Hz), 4.68, 4.82 (each 1H, s), 4.93 (1H, overlapped), 5.33 (1H, d, J =5.2 Hz), 5.81 (1H, s), 6.34 (1H, s); ^{13}C-NMR (pyridine d_5) Table 1.

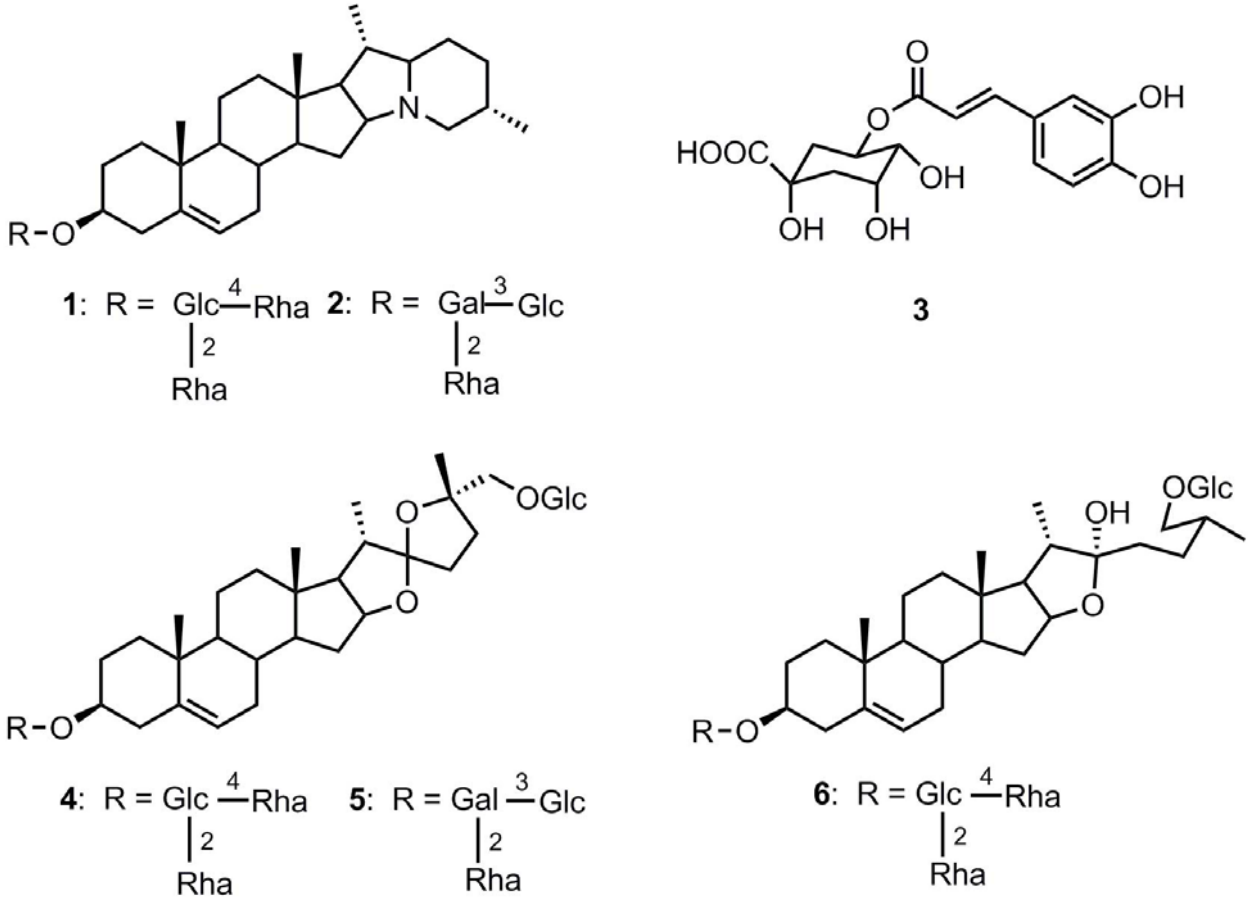

Fig 2: Structures of isolated compounds

2.5. α-Solanine (2)

A white amorphous powder; $[\alpha]_D^{30}$ -33°(*c* 0.54, MeOH) , ^{1}H-NMR (pyridine d_5) δ: 0.83 (3H, d, *J* =6.6 Hz), 0.96 (3H, brd), 1.05 (3H, s), 1.06 (3H, s), 1.70 (3H, d, *J* =6.2 Hz), 4.92 (2H, m), 4.93 (1H, d, *J* =7.7 Hz), 5.19 (1H, d, *J* =8.1 Hz), 5.36 (1H, brs), 6.29 (1H, s); ^{13}C-NMR (pyridine d_5) Table 1.

2.6. Chlorogenic acid (3)

A white amorphous powder; $[a]_D^{21}$ - 21.0º (*c* 0.46, H_2O); ^{1}H-NMR (CD_3OD+D_2O) δ 7.57 (1H, d, *J* = 15.8 Hz, H-7'), 7.09 (1H, s, H-2'), 6.98 (1H, d, *J* = 7.9 Hz, H-6'), 6.85 (1H, d, *J* = 7.9 Hz, H-5'), 6.32 (1H, d, *J* = 15.8 Hz, H-8'), 5.36 (1H, m, H-5), 4.30 (1H, brs, H-3), 3.85 (1H, brd, *J* = 9.7 Hz, H-4), 2.1-1.8 (4H, m, H-2,6); ^{13}C-NMR (CD_3OD+D_2O) δ 180.7 (C-7), 169.6 (C-9'), 148.5 (C-4'), 147.1 (C-7'), 145.7 (C-3'), 127.7 (C-1'), 123.3 (C-6'), 116.8 (C-5'), 115.6 (C-8'), 115.2 (C-2'), 78.9 (C-1), 73.9 (C-4), 72.3 (C-3), 71.9 (C-5), 39.6 (C-6), 37.9 (C-2).

Table 1: ^{13}C-NMR data of compounds **1**, **2**, **4**, **5** and **6** in Pyridine-d_5

C. No.	1	2	4	5	6
1	37.2	37.4	37.4	37.4	37.4
2	31.5	32.2	30.0	30.0	30.1
3	77.8	77.4	77.7	77.4	78.4
4	39.8	39.9	39.7	39.8	38.9
5	140.5	140.8	140.7	140.8	140.7
6	121.4	121.6	121.7	121.7	121.7
7	32.0	32.6	32.2	32.2	32.2
8	31.0	31.5	31.5	31.6	31.6
9	49.8	50.2	50.1	50.2	50.3
10	36.9	37.0	37.0	37.0	37.0
11	20.7	21.0	21.0	21.0	21.1
12	38.6	38.7	38.8	38.7	39.8
13	40.2	40.4	40.4	40.4	40.7
14	57.2	57.5	56.5	56.5	56.5
15	26.0	27.0	32.2	32.2	32.4
16	69.2	69.3	80.6	80.7	81.0
17	61.0	62.3	62.8	62.8	63.7
18	16.3	16.6	16.0	16.1	16.4
19	19.0	19.2	19.3	19.3	19.3
20	36.4	36.6	38.5	38.5	40.6
21	18.2	19.1	15.3	15.3	16.4
22	75.0	74.9	120.0	120.0	110.6
23	27.8	29.5	33.4[a]	33.5[a]	30.1
24	29.8	29.8	33.8[a]	33.9[a]	28.2
25	28.8	30.0	83.4	83.5	34.3
26	58.7	59.6	75.7	75.5	75.3
27	19.0	19.2	26.7	26.7	17.3
	Glc	**Gal**	**Glc**	**Gal**	**Glc**
1	100.3	100.3	100.1	100.3	100.2
2	78.8	76.3	79.0	76.4	78.0[a]
3	76.8	84.8	76.6	84.7	76.8
4	77.8	70.2	77.8	70.3	77.0[a]
5	78.2	74.8[a]	78.1	73.8	77.8[a]
6	62.3	62.3	61.4	62.4[a]	61.2
	2-Rha	**2-Rha**	**2-Rha**	**2-Rha**	**2-Rha**
1	102.0	102.0	101.9	102.1	101.9
2	72.4[a]	72.4	72.4[a]	72.5[b]	72.4
3	72.7[a]	72.7	72.7[a]	72.8[b]	72.6[b]
4	74.0	74.0	73.9	74.1	74.0[c]
5	69.3	69.3	69.4	69.4	69.4[d]
6	18.5	18.5[b]	18.3[b]	18.6	18.4[e]
	4-Rha	**3-Glc**	**4-Rha**	**3-Glc**	**4-Rha**
1	102.9	105.7	102.7	105.7	102.0
2	72.4[a]	74.9[a]	72.4[a]	75.0	72.4
3	72.4[a]	78.3	72.6[a]	78.5	72.7[b]
4	73.7	71.4	73.7	71.5[c]	73.8[c]
5	70.1	78.2	70.2	78.4[d]	70.3[d]
6	18.5	62.4[b]	18.5[b]	62.5[a]	18.5[e]
			26-Glc	**26-Glc**	**26-Glc**
1			105.0	105.1	105.0
2			75.1	75.2	75.1
3			78.4	78.5	78.5
4			71.5	71.6[c]	71.6
5			77.9	78.5[d]	78.5
6			62.6	62.7[a]	62.7

[a-e] Assignments with same superscripts may be reversed in column.

2.7. Aculeatiside A (4)

A white amorphous powder; $[\alpha]_D^{30}$ -86.1° (*c* 0.72, MeOH), ^{1}H-NMR (pyridine d_5) δ: 0.81 (3H, s), 1.05 (3H, s), 1.15 (3H, d, *J* =6.6 Hz), 1.52 (3H, s), 1.62 (3H, d, *J* =5.9 Hz s), 1.76 (3H, d, *J* =5.9 Hz), 4.92 (2H, d, J=7.7 Hz), 5.32 (1H, brs), 5.84 (1H, s), 6.38 (1H, s); ^{13}C-NMR (pyridine d_5) Table 1.

2.8. Aculeatiside B (5)

A white amorphous powder; $[\alpha]_D^{30}$ -57.4°(*c* 0.75, MeOH), ^{1}H-NMR (pyridine d_5) δ: 0.81 (3H, s), 1.05 (3H, s), 1.15 (3H, d, *J* =6.6 Hz), 1.52 (3H, s), 1.62 (3H, d, *J* =5.9 Hz s), 1.76 (3H, d, *J* =5.9 Hz), 4.94 (1H, d, *J* =7.7 Hz), 5.26 (1H, d, *J* =7.7 Hz), 5.32 (1H, brs), 6.29 (1H, s); ^{13}C-NMR (pyridine d_5) Table 1.

2.9. Protodioscin (6)

A white amorphous powder; $[\alpha]_D^{30}$ -86.1° (*c* 0.72, MeOH), ^{1}H-NMR (pyridine d_5) δ: 0.90 (3H, s), 1.07 (3H, s), 1.64 (3H, d, *J* =6.2 Hz s), 1.77 (3H, d, *J* =6.2 Hz), 4.95 (1H, d, J=6.2 Hz), 5.86 (1H, s), 6.40 (1H, s); ^{13}C-NMR (pyridine d_5) Table 1.

3. Results and Discussion

In the present study, we have isolated and identified major steroidal glycosides from the fresh unripe fruits, aerial parts and tubers of potato. Two steroidal alkaloid glycosides: α-chaconine (**1**), α-solanine (**2**), [4, 5] and a phenolic compound, chlorogenic acid (**3**) [6] were isolated from the fresh unripe fruits of potato. Two steroidal alkaloid glycosides: α-chaconine (**1**), α-solanine (**2**) and two steroidal glycosides; aculeatiside A (**4**), aculeatiside B (**5**) [7] were isolated from aerial parts. From the tubers, two steroidal alkaloid glycosides: α-chaconine (**1**), α-solanine (**2**) and one steroidal glycoside: protodioscin (**6**) [8] were isolated. The structures of these compounds (Fig. 2) were elucidated on the basis of their physical and spectroscopic data (Table 1) and comparison with reported literature values.

The presence of steroidal alkaloid glycosides in different plants parts of potato is well studied specially in aerial parts and tubers. In case of tuber flesh, the content of these glycosides is usually very low, but may increase with exposure to light or injury [1]. Thus, greened potato tubers may be toxic. In this study, we isolated α-chaconine (**1**) and α-solanine (**2**), the major solanaceous steroidal alkaloid glycosides from fresh unripe fruits and aerial parts. Thus, these fruits and aerial parts are unsuitable for consumption.

4. References

1. Dewick PM. Medicinal Natural Products: A Biosynthetic Approach, Edn 3, John Wiley & Sons, Ltd, Chichester, 2009, 410.
2. Friedman M. Potato glycoalkaloids and metabolites: Roles in the plant and in the diet. Journal of Agricultural and Food Chemistry 2006; 54:8655.
3. Zhang ZQ, Luo JG, Wang JS, Kong LY. Five new steroidal alkaloid glycosides from *Solanum tuberosum*. Helvetica Chimica Acta 2013; 96:931.
4. Mahato SB, Sahu NP, Ganguly AN, Kasai R, Tanaka O. Steroidal alkaloids from *Solanum khasianum*: Application of *13*C NMR spectroscopy to their structure elucidation. Phytochemistry 1980; 19:2017.
5. Zhao JM, Li SY, Zhou YF, Zhang LP, Zhou DW. Antifungal activity of five solanaceous glycoalkaloids and their mixtures against phytopahtogenic fungi *Cercosporella brassicae* and *Alternaria porri*. Chemical Research in Chinese Universities 2006; 22:189.
6. Ono M, Masuoka C, Tanaka T, Ito Y, Nohara T. Antioxidative and antihyaluronidase activities of some constituents from the aerial parts of *Daucus carota*. Food Science and Technology Research 2001; 7:307.
7. Saijo R, Fuke C, Murakami K, Nohara T, Tomomatsu T. Two steroidal glycosides, aculeatiside A and B from *Solanum aculeatissimum*. Phytochemistry 1983; 22:733.
8. Ikeda T, Tsumagari H, Okawa M, Nohara T. Pregnane- and furostane-type oligoglycosides from the seeds of *Allium tuberosum*. Chemical and Pharmaceutical Bulletin 2004; 52:142.