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A Hemiterpenoid Glucoside from *Musa paradisiaca*

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From flower buds of *Musa paradisiaca* a new hemiterpenoid glucoside named 1,1-dimethylallyl alcohol β-glucoside was isolated together with 3 known compounds, benzyl alcohol glucoside, syringin and (*6S,9R*)-roseoside. The structures of these compounds were elucidated on the basis of spectroscopic data.

Keywords: *Musa paradisiaca*; Musaceae; hemiterpenoid glucoside; dimethylallyl glucoside; roseoside

Musa paradisiaca Linn. (family Musaceae) is a plant cultivated widely in the Philippines, in many forms and varieties, which was probably introduced originally from Malaya and other tropical Asian countries. The inflorescence of this plant is widely used as a vegetable, and the fruit is very popular as food. *M. paradisiaca* is also well known for its medicinal properties: the sap of the trunk, which is astringent and styptic is used for the treatment of diarrhea and dysentery, the root as antifebrile and restorative, and the cooked flowers and fruits for the treatment of diabetes mellitus and peptic and duodenal ulcers.[1] Pharmacological studies showed that the pulp powder of this plant has a significant anti-ulcerogenic activity in rats and guinea pigs.[2-4]

Previous investigations had revealed that *M. paradisiaca* contained some sterols, triterpenes, and several phytoalexins.[5-10] The present paper describes the isolation of a new hemiterpenoid glucoside named 1,1-dimethylallyl alcohol β-glucoside (**1**) together with 3 known compounds, benzyl alcohol glucoside (**2**), syringin (**3**) and (*6S,9R*)-roseoside (**4**) from the flower buds of this plant. It also describes structural elucidation of this new compound.

EXPERIMENTAL

Mp: uncorr. Optical rotations were measured on a Union PM-101 automatic digital polarimeter, NMR, on a JEOL JNM A-500 with TMS as int. standard, and mass spectra on a JEOL JMS-SX102 spectrometer by the direct inlet method. HPLC was carried out by using a D-ODS-5 column (20.0 mm i.d. x 25 cm) with a Toyo Soda high speed chromatograph HLC-803D pump and a Toyo Soda RI-18 differential refractometer as detector, at the flow rate of 6 ml/min. For column chromatography, Diaion HP-20 (Mitsubishi), Kiesel gel 60 (70-230 mesh, Merck) and LiChroprep RP-18 (Merck) were used. For TLC, precoated silica gel 60 plates, F-254 (Merck) and precoated RP-18 plates, F-254 (Merck) were used.

Plant Material. Flower buds of *Musa paradisiaca var.* San Juan were collected in the province of Cagayan, Philippines in February ~ May 1996 and authentication was done by Dr. Norma Orlido-Aguilar of the Plant Biology Division, Institute of Biological Sciences, CAS, UPLB, Philippines. A voucher specimen is deposited at the Department of Medicinal Chemistry and Natural Products, Institute of Pharmaceutical Sciences, Hiroshima University School

of Medicine, Hiroshima, Japan.

Extraction and isolation of constituents of M. paradisiaca. 1 kg of air-dried, powdered flower buds of *M. paradisiaca* was extracted with MeOH (4l, 4 times) at room temp. The combined MeOH extracts were evaporated under reduced pressure. The residue (110 g) was suspended in H_2O and then successively treated with *n*-C_6H_{14}, EtOAc and *n*-BuOH to give 65 g, 11 g and 8 g of the extracts, respectively. The *n*-BuOH extract was repeatedly subjected to silica gel CC [CH_2Cl_2-MeOH-H_2O (30:1:0.1 → 10:1:0.1)] followed by Sephadex LH-20 CC (80% MeOH) then repeated HPLC (20% MeOH) to afford 4 compounds, **1** (8 mg), **2** (7 mg), **3** (7 mg) and **4** (6mg).

1,1-Dimethylallyl alcohol β-glucoside (**1**). White powder. $[\alpha]_D^{21}$ –25.3° (MeOH, *c* = 0.51). FAB-MS (negative) *m/z* 247 $[C_{11}H_{20}O_6\text{-H}]^-$. ^{1}H- and ^{13}C-NMR: see Table.

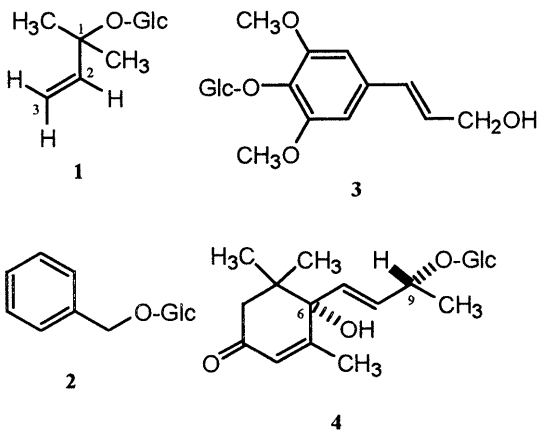
Benzyl alcohol glucoside (**2**). Colorless crystals from aq-MeOH. $[\alpha]_D^{21}$ –61.1° (MeOH, *c* = 0.54), *lit.*[11] –59.2 °. mp 122-124°, *lit.*[11] 123–124°. NMR: identical with literature value.[11]

Syringin (**3**). Colorless needles. mp 191-193°, *lit*[12]. 187–188°. NMR: identical with literature value.[12]

(6S,9R)-Roseoside (**4**). White powder. $[\alpha]_D^{21}$ +107.3° (MeOH, *c* = 0.23). FAB-MS (negative) *m/z* 385 $[C_{19}H_{30}O_8\text{-H}]^-$. ^{1}H-NMR (DMSO-$d_6$) δ: 2.14 (1H, *brd*, *J* = 16.8 Hz, H-2_a), 2.51 (1H, *brd*, *J* = 16.8 Hz, H-2_b), 5.86 (1H, *q*, *J* = 1.2 Hz, H-4), 5.848 (1H, *d*, *J* = 1.4 Hz, H-7), 5.851 (1H, *d*, *J* = 3.9 Hz, H-8), 4.41 (1H, *qdd*, *J* = 6.4, 1.4, 3.9 Hz, H-9), 1.28 (3H, *d*, *J* = 6.4 Hz, H-10), 1.02 (3H, *s*, H-11), 1.03 (3H, *s*, H-12), 1.91 (3H, *d*, *J* = 1.2 Hz, H-13), 4.34 (1H, *d*, *J* = 7.8 Hz, H-1'). ^{13}C-NMR (DMSO-d_6) δ: 42.4 (C-1), 50.7 (C-2), 201.2 (C-3), 127.2 (C-4), 167.3 (C-5), 80.0 (C-6), 131.6 (C-7), 135.3 (C-8), 77.3 (C-9), 21.2 (C-10), 23.4 (C-11), 24.7 (C-12), 19.6 (C-13), 102.7 (C-1'), 75.3 (C-2'), 78.1 (C-3') 71.7 (C-4'), 78.0 (C-5'), 62.8 (C-6').

RESULTS AND DISCUSSION

From a MeOH extract of dried, ground flower buds of *Musa paradisiaca var.* San Juan four compounds, **1-4** were obtained. Compounds **2** and **3** were identified as benzyl alcohol glucoside[11] and syringin,[12] respectively, and **4** as roseoside which was first isolated from *Vinca rosea* by Bhakuni and co-workers in 1974.[13] Roseoside is known to have four diastereomers.[14-17] The ^{1}H- and ^{13}C-NMR spectral data of **4** were superimposable on those of *(6S,9R)*-roseoside, and their optical rotations were also in good agreement. Thus, the configuration of **4** was determined to be *(6S,9R)*.



Compound **1** exhibited a quasi-molecular ion peak $[M\text{-H}]^-$ at *m/z* 247 (negative ion FAB-MS spectrum) corresponding to the molecular formula $C_{11}H_{20}O_6$.

The ^{1}H- and ^{13}C-NMR spectra of **1** (table below) showed that **1** had a glucose unit with a β-configuration based on the coupling constant, ($J_{1,2}$ = 7.6 Hz), two methyls, one quaternary carbon with oxygen function and a monosubstituted double bond. On the basis of these data, the structure of **1** was elucidated as 1,1-dimethylallyl alcohol β-glucoside as shown in the figure. Compound **1** is a new natural product.

NMR Spectral Data of Compound **1**
(125 and 500 MHz, in DMSO-d_6)

	^{13}C	^{1}H
1	76.9	
2	144.5	5.98, 1H, *dd* (11, 17.7)
3	112.9	5.17, $1H_a$, *dd* (1, 17.7)
		5.03, $1H_b$, *dd* (1, 11)
CH_3	27.4	3.27, 3H, *s*
CH_3	25.9	3.27, 3H, *s*
Glc-1'	98.0	4.23, 1H, *d* (7.6)
2'	73.4	
3'	76.6	
4'	70.2	
5'	76.5	
6'	61.1	

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