

A New Acyclic Sesquiterpene Oligoglycoside from Pericarps of *Sapindus mukurossi*

Jie Ru SUN^{1,2*}, Kong Chang CHENG¹, Tie Yin PAN¹, Xin Mei SI¹

¹East China University of Science and Technology, Shanghai 200237

²Shanghai Whitecat Company Ltd., Shanghai 200231

Abstract: A new acyclic sesquiterpene oligoglycoside, named mukurozioside **A**, was isolated from pericarps of *Sapindus mukurossi*. On the basis of chemical and spectral evidence, the structure of mukurozioside **A** has been established as: 11(S)-2, 6(E, E)-dodecadiene-3, 7, 11-trimethyl-, 12-diol-1, 12-bis-O- β -L-rhamnopyranosyl-(1 \rightarrow 2)-[β -L-rhamnopyranosyl-(1 \rightarrow 3)]-6-O-acetyl- β -D-Glucopyranoside (**1**).

Keywords: *Sapindus mukurossi*, sesquiterpene oligoglycoside, mukurozioside **A**.

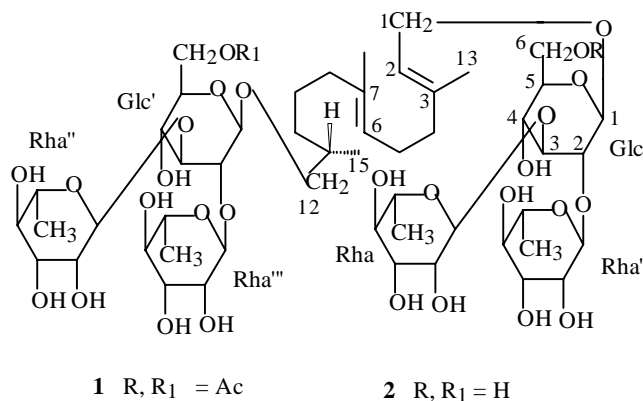
The pericarps of *Sapindus mukurossi* (Chinese name: Wuhuanzi) is used as a source of natural surfactant and an expectorant in traditional chinese medicine. From the pericarps of this plant, seven saponins and four sesquiterpene oligoglycosides were reported previously¹⁻³. Recently, from this source, we have isolated a new acyclic sesquiterpene oligoglycoside, named mukurozioside **A** (**1**).

Mukurozioside **A** (**1**), an amorphous powder, $[\alpha]_D^{25}$ -65.53 (c 1.0, MeOH), has a molecular formula C₅₅H₉₂O₃₀ determined from its ESI-MS (m/z 1255 [M+Na]⁺) and ¹³CNMR data. Its IR showed characteristic absorptions at 3415 (OH), 1727 (ester) and 1640 cm⁻¹ (C=C). The ¹HNMR and ¹³CNMR of **1** indicated the presence of two trisubstituted double bonds [two olefinic protons: δ_H 5.32, 5.03 (each 1H, t, J=6Hz); two olefinic methyls: δ_H 1.61, 1.51 (each 3H, s) and four olefinic carbons: δ_C 121.1, 125.0, 136.4, 142.3], a secondary methyl (0.82, 3H, d, J=6Hz) and two acetyl groups [δ_H 2.01 (6H, s) and δ_C 21.1, 20.8; 172.7, 172.7]. Its spectral features suggested **1** to be an acyclic sesquiterpene oligoglycoside. Comparison of the ¹HNMR and ¹³CNMR of **1** with those of mukurozioside II **a** (**2**)² indicated that **1** has the same aglycone, mukurozidiol², as **2**. Comparing the ¹³CNMR of the aglycon part of **1** with that of mukurozidiol, the downfield shifts of C₁ and C₁₂ (6.9 and 8.1 ppm) indicated that C₁ and C₁₂ of aglycone of **1** were glycosylated. Acid hydrolysis of **1** produced sugar components identified as D-glucose and L-rhamnose (1:2) based on GC/MS analysis. Comparison of the ¹³CNMR signals of the sugar parts of **1** (**Table 1**) with those of **2**² revealed that **1** has the same sugar parts as **2** except for the presence of two acetyl groups.

Table 1 ^{13}C NMR data of compounds **1** (CD_3OD , in ppm)

| aglycon moiety | | | | sugar moiety | | | | | | | |
|----------------|-------|----|------|-----------------|-------|-------|-------|-------|-------|--------|--|
| C | | C | | C | Glc | Glc' | Rha | Rha' | Rha'' | Rha''' | |
| 1 | 66.3 | 9 | 26.3 | 1 | 101.2 | 103.2 | 103.7 | 103.1 | 103.7 | 102.5 | |
| 2 | 121.1 | 10 | 34.4 | 2 | 80.3 | 79.2 | 72.2 | 72.2 | 72.2 | 72.2 | |
| 3 | 142.3 | 11 | 34.7 | 3 | 87.9 | 88.3 | 72.1 | 72.1 | 72.1 | 72.1 | |
| 4 | 40.7 | 12 | 76.6 | 4 | 70.1 | 70.1 | 73.5 | 73.5 | 73.5 | 73.5 | |
| 5 | 27.3 | 13 | 16.1 | 5 | 77.5 | 77.6 | 70.7 | 70.5 | 70.7 | 70.5 | |
| 6 | 125.0 | 14 | 16.1 | 6 | 62.5 | 62.5 | 18.3 | 18.3 | 18.0 | 18.0 | |
| 7 | 136.4 | 15 | 17.4 | CH ₃ | 21.1 | 20.8 | | | | | |
| 8 | 41.1 | | | C=O | 172.7 | 172.7 | | | | | |

On the basis of the assigned protons of **1**, its ^{13}C NMR resonances of each sugar unit were identified by HMQC and further confirmed by HMBC. From the HMBC spectrum of **1**, cross peaks were observed between C_1 (66.3) and $\text{H}_{\text{Glc}1}$ (4.38, d, $J=7.7\text{Hz}$), $\text{C}_{\text{Glc}2}$ (80.3) and $\text{H}_{\text{Rha}1}$ (4.92), $\text{C}_{\text{Glc}3}$ (87.9) and $\text{H}_{\text{Rha}1}$ (4.90), C_{12} (76.6) and $\text{H}_{\text{Glc}1}$ (4.33, d, $J=7.6\text{Hz}$), $\text{C}_{\text{Glc}2}$ (79.2) and $\text{H}_{\text{Rha}''1}$ (5.01), $\text{C}_{\text{Glc}3}$ (88.3) and $\text{H}_{\text{Rha}''1}$ (4.90), $\text{C}_{172.7}$ (C=O of acetyl) and $\text{H}_{\text{Glc}6}$ (3.69; 3.84), $\text{C}_{172.7}$ (C=O of acetyl') and $\text{H}_{\text{Glc}6}$ (3.69; 3.84). Thus, mukurozioside **A** was determined to be 11(S)-2, 6(E, E)-dodecadiene-3, 7, 11-trimethyl -1,12-diol-1,12-bis-O- -L-rhamnopyranosyl-(1 \rightarrow 2)-[-L-rhamnopyranosyl-(1 \rightarrow 3)]-6-O-acetyl- β -D-glucopyranoside(**1**).

Figure 1 Structure of mukurozioside **A** (**1**) and mukurozioside **II a** (**2**)

References

1. H. Kimata, T. Nakashima, S. Kokubun, K. Nakayama, Y. Mitoma, T. Kitahara, N. Yata, O. Tanaka, *Chem. Pharm. Bull.*, **1983**, 31 (6), 1998.
2. R. Kasai, H. Fujino, T. Kuzuki, W. H. Wong, C. Goto, N. Yata, O. Tanaka, F. Yasuhara, S. Yamaguchi, *Phytochemistry*, **1986**, 25 (4), 871.
3. I. Azhar, K. Usmanhani, S. Perveen, M. S. Ali, V. U. Ahmad, *Pak. J. Pharm. Sci.*, **1993**, 6 (2), 71.

Received 13 September, 2001