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# Polyoxygenated *seco*-cyclohexenes and other constituents from *Uvaria valderramensis*

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ABSTRACT

Phytochemical study on the Philippine endemic Annonaceae plant *Uvaria valderramensis* afforded a new highly oxygenated *seco*-cyclohexene derivative, valderepoxide (**1**), along with the six known compounds uvamalols D (**2**) and G (**3**), grandiuvarone (**4**), 2′-hydroxy-3′,4′,6′-trimethoxychalcone (**5**), valderramenol B (**6**) and benzoic acid. The structure of **1** was determined through extensive spectroscopic analyses including 1D, 2D NMR and HRESIMS. Its relative stereochemistry was established using 2D-NOESY. This is the first report on the isolation of polyoxygenated compounds **1**–**3** and chalcone **5** from *U. valderramensis*.

## 1. Subject and source

The genus *Uvaria* Linn (Annonaceae) is a species-rich genus with around 210 known species of woody climbers and scandent shrubs commonly occurring in wet tropical forests of Africa, Madagascar, continental Asia, Malesia, Northern Australia and Melanesia (Zhou et al., 2012). According to Merrill (1923), the genus is widely distributed with most of its species considered to be endemic to the Philippines. Among the listed distribution sites of the genus, the municipality of Valderrama in Antique Province, Philippines is known to have the endemic species, *Uvaria valderramensis* Cabuang, Exconde & Alejandro (Cabuang et al., 2012).

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*Uvaria valderramensis* (leaves) was collected from Brgy. Bugnay, Valderrama, Antique Province (July of 2013) and identified by one of the authors (G. J. D. Alejandro). A voucher specimen is deposited at the herbarium of the UST Research Center for the Natural and Applied Sciences (voucher no. USTH 0012).

## 2. Previous work

Initial phytochemical studies reported the isolation of two new tetrahydroxanthenedione derivatives along with the oxepinone compound grandiuvarone and the tetrahydrobenzylisoquinoline alkaloid reticuline (Macabeo et al., 2014).

## 3. Present study

The air-dried powdered leaves (7.80 kg) was percolated with 1:1 dichloromethane-MeOH (84 L). The dichloromethane-methanolic extracts were combined and evaporated to dryness under vacuum at 45 °C to yield a green syrup (1.20 kg). The extract was suspended in water and extracted with petroleum ether (16.5L). The petroleum ether sub-extract was set aside and the aqueous layer was extracted with dichloromethane (19.7 L). The dichloromethane layer was dried over anhydrous $Na_2SO_4$ and evaporated to dryness to afford a brownish syrup (360 g). This was subjected to vacuum liquid column chromatography using silica gel and eluted with increasing gradients of EtOAc in petroleum ether (20%) and MeOH in EtOAc (20%). Fractions were collected and pooled into seven fractions on the basis of TLC. Fraction 2 (70 g) was further subjected to vacuum liquid column chromatography using silica gel and eluted with EtOAc in petroleum ether (10%) and MeOH in EtOAc (10%). Sub-fraction 3 (6.1 g) was subjected to silica gel column chromatography (3×) using hexane-EtOAc-DCM (5:2:1) to give benzoic acid and **4** (1.07 g). Rechromatography of the remaining (combined) fractions using the same solvent system afforded **1** (10.0 mg), **2** & **3** (6.0 mg, 1:3), **5** (18.0 mg), and **6** (7.0 mg) (Fig. 1).

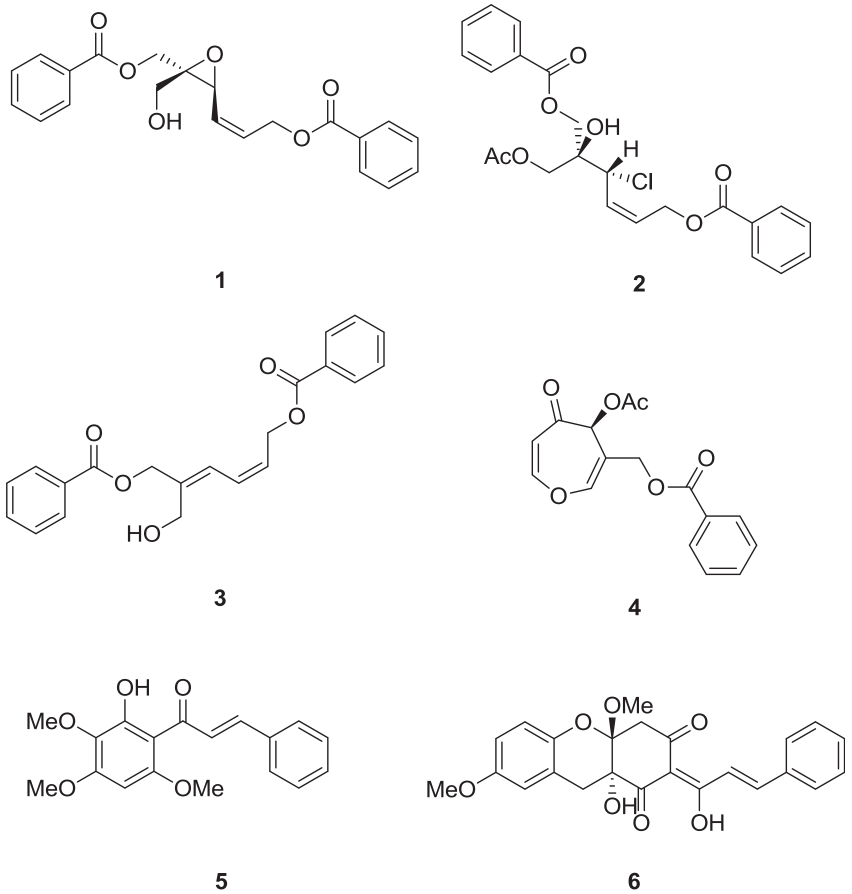

**Fig. 1.** Structure of the isolated compounds from *U. valderramensis*.