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Insecticidal activity of sesquiterpene lactones and monoterpenoid from the fruits of *Carpesium abrotanoides*

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ABSTRACT

The isolation of secondary metabolites produced by plants can lead to the discovery of new insecticidal agents. The aim of this study was to identify secondary metabolites from the fruits of *Carpesium abrotanoides*, a well-known medicinal and poisonous plant belonging to the family Asteraceae, with the potential to act as natural insecticides. Two new sesquiterpene lactones 9β-hydroxy-1βH, 11αH-guaia-4,10(14)-dien-12,8α-olide (**1**) and 9β-hydroxy-1βH, 11βH-guaia-4,10(14)-dien-12,8α-olide (**2**) along with four known sesquiterpene lactones (**3**-**6**) and one monoterpenoid (**7**) have been isolated. The structures of these compounds were established on the basis of 1D and 2D NMR data and HRESIMS data interpretation. To characterize their insecticidal activities, bioassays were conducted using two insect pest species of agricultural importance. Compounds **1**–**7** showed antifeedant effects to 3rd instar larvae of *Plutella xylostella* (Lepidoptera: Plutellidae) in a concentration-dependant manner with EC_{50} of 19.84, 42.82, 97.94, 96.90, 39.94, 37.35 and 43.99 mg/L, respectively. Moreover, all of these compounds display stomach-contact combination toxicity toward 4rd instar larvae of *Bradysia odoriphaga* Yang and Zhang (Diptera: Sciaridae) (LD_{50} = 18.71, 80.29, 230.65, 319.67, 31.18, 40.87 and 68.47 mg/L, respectively). In general, this is the first report of insecticidal activities of secondary metabolites isolated from *C. abrotanoides*. Moreover, compound **1** showed the best insecticidal activity in the test, demonstrating its potential to be used as a natural insecticides.

1. Introduction

Although a wide variety of synthetic insecticides were used to control pests, repeat application of those agrochemicals over years has led to the development of resistance in pest populations and environmental problems by their potential effect upon non-target organisms, including humans. Currently the demand for more eco-friendly chemicals to be used in integrated pest management is growing (Pavela, 2015). Since plant secondary metabolites result from the interaction between plants and the environment (life and nonlife) during the long period of plants evolution, they are not only effective against different types of pests, but also effective in reducing the risk of environmental toxicity (Regnault-Roger et al., 2012; Kato-Noguchia et al., 2013; Araniti et al., 2013). In light of this possibility, plant secondary insecticidal metabolites have been isolated and identified from numerous plant species (Mann and Kaufman, 2012). For instance, some botanical insecticides, such as nicotine, pyrethrum, and neem extracts, are made as defenses against insect pests (Franck et al., 2009; Cantrell et al., 2012).

The genus *Carpesium* belonging to the family Asteraceae, includes approximately 21 species worldwide, which are mostly perennial herbs, and distributed across Asia and Europe, particularly in the mountainous areas of Southwest China. This genus is well documented as a good source of sesquiterpenoids and monoterpenoids (Zhang et al., 2015), two of which are the most abundant and structurally diverse group of secondary metabolites with biological activities in plants, and play important roles in plant-insect interactions (Cheng et al., 2007).

Carpesium abrotanoides, a well-known poisonous plant, is widely distributed in China and Eastern Asia. It is reported that this plant synthesizes secondary metabolites with diverse pharmacological properties, including antifungal, antibacterial, antineoplastic, anti-inflammatory, and cytotoxic activities (Zhang et al., 2015). Its aerial parts have been used traditionally in Chinese, Japanese, and Korean as insecticides and to treat bruises and fever (Wang et al., 2009). Meanwhile, the fruits of *C. abrotanoides* is called

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"Bei-He-Shi" by local people in China, describing it is an insecticide and used for the treatment of tapeworm and roundworm in folk medicine (Zhang et al., 2015; Wang et al., 2009; Liu et al., 2015). *C. abrotanoides* are officially recorded and defined as low toxicity to human (Liu et al., 2014) even if large doses are given, inducing adverse drug reactions slowly or mildly, according to the Chinese Pharmacopoeia 2010 (Chinese Pharmacopoeia Commission, 2010). Therefore, it is cultivated in the northwest area in China as sources of medicinal plants. However, the whole plant has been traditionally used as homemade insecticide for controlling vegetable insect pests, such as *Pieris rapae, Euxoa segetum* and so on. Furthermore, the whole plants of *C. abrotanoides* were put into the grain depot to control the stored product insect pests, like *Sitophilus zeamais* and *Tribolium castaneum* in China (Tang and Liu, 2002).

More recently, extracts derived from *C. abrotanoides* have been proved to show insecticidal activities against different pest species, such as antifeedant efficacy against *Spodoptera exigua* (Feng et al., 2012), contact toxicities against *Sitophilus Zeamais* (Ma et al., 2013), killing effect on *Taenia asiatica* Cysticercus (Liu et al., 2015), antifeedant activity and contact toxicity against *Mythimna separata* and *Plutella xylostella* (Li et al., 2012).

Although there should be possible relationship between the secondary metabolites in *C. abrotanoides* and its plant defenses effect, to our knowledge, studies on the secondary metabolites with insecticidal activities from *C. abrotanoides* are not yet available. The present study is to verify the potential use of its secondary metabolites in the development of botanical insecticides. As a result, six sesquiterpene lactones, including two new sesquiterpene lactones, as well as one monoterpenoid were isolated and identified from the fruits of *C. abrotanoides*, meanwhile the compounds bioactivities against two insect pest species is characterized for the first time. *Plutella xylostella* (Lepidoptera: Plutellidae) was a model of insect pest. Another pest *Bradysia odoriphaga* Yang and Zhang (Diptera: Sciaridae) chosen here, was the major insect pest affecting Chinese chive in Northern China, which attacks 20–30% of Chinese chives and causes 30–80% production losses (Zhang et al., 2014). Except for Chinese chive, the insect feeds on seven plant families and more than thirty plants species, including welsh onion, garlic, onion (all Liliaceae), cucumber (Cucurbitaceae), Chinese cabbage (Cruciferae), and lettuce (Asteraceae), and also causes production losses in mushroom sheds. Its larvae tend to aggregate in fields and directly damage the above plants by feeding on root and corm tissue in the growing medium, which disrupts the uptake of water and nutrients in the plants, whereas its adults can cause minimal direct plant damage (Lu et al., 2006). Since the larva always gather in the roots and stems of the plant, it is hard to be controlled with common strategies. Chemigation was a traditional method to control this pest, a mass of pesticides was needed due to the dilution effects of water and soil on pesticides (Jiang et al., 2004). Generally, organophosphate insecticides, such as chlorpyrifos and phoxim, are the main method to control the pests of Chinese chives. Worst of all, phorate and methamidophos which are banned in some parts of the world were used to control the *B. odoriphaga* (Liu et al., 2013). However in recent years the residual toxicity of organophosphate insecticides led to the increasing calls for new and less poisonous approaches to control this pests (Chen et al., 2015).

2. Materials and methods

2.1. Instruments

1D and 2D NMR spectra were recorded on a Bruker AV-600 spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C, respectively), using tetramethylsilane (TMS) as an internal standard. HRESIMS were measured by an Agilent 6520 Q-TOF LC–MS mass spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. IR data were recorded using a Nicolet Magna-IR 750 spectrophotometer. Analytical and preparative TLC were run on silica gel plates (GF_{254}, Yantai Institute of Chemical Technology, China). Spots were observed under UV light and visualized by spraying with 10% H_2SO_4, followed by heating. Column chromatography was performed on silica gel (SiO_2, 100–200 mesh and 200–300 mesh, Qingdao Marine Chemical Factory, China) and Sephadex LH-20 (Amersham Biosciences).

2.2. Plant material preparation

The air-dried fruits of *Carpesium abrotanoides* were collected in Tianquan, Sichuan Province, P. R. China, in July, 2013. It was identified by Professor Lin Yang (College of Life and Environmental Sciences, Minzu University of China). A voucher specimen (NO. 20130702) was deposited in the herbarium of the College of Life and Environmental Sciences, Minzu University of China.

2.3. Extraction and isolation

The air-dried fruits of (450 g) of *C. abrotanoides* were pulverized and extracted with methanol (15 L) at room temperature for 7 d each time. The extracts were combined and evaporated under vacuum. The residue (31.5 g) was subjected to silica gel column chromatography (100–200 mesh, 80 cm × 8 cm, 2000 g) eluting with petroleum ether, gradually increasing polarity with acetone to afford 7 fractions: Fr. A (petroleum ether-acetone, 15:1), Fr. B (petroleum ether-acetone, 10:1), Fr. C (petroleum ether-acetone, 8:1), Fr. D (petroleum ether-acetone, 5:1), Fr. E (petroleum ether-acetone, 3:1), Fr. F (petroleum ether-acetone, 2:1), Fr. G (petroleum ether-acetone, 1:1). Fr. B (2.8 g) was further purified by silica gel column chromatography (200–300 mesh, 50 cm × 3 cm, 400 g, petroleum ether-$CHCl_3$, 8:1) to give compound **6** (20.2 mg). Fr. C (3.6 g) was further purified by silica gel column chromatography (200–300 mesh, 50 cm × 4 cm, 600 g, petroleum ether-$CHCl_3$, 5:1) to give Fr. C1 and Fr. C2. Fr. C1 (0.4 g) was further purified by silica gel column chromatography (200–300 mesh, 50 cm × 2 cm, 120 g, petroleum ether-ethylacetate, 3:1) to give compound **3** (7.2 mg) and compound **4** (11.4 mg). Fr. C2 (0.2 g) was further purified by silica gel column chromatography (200–300 mesh, 50 cm × 2 cm, 120 g, $CHCl_3$-ethylacetate, 3:2) to give compound **1** (2.2 mg) and compound **2** (2.8 mg). Fr. D (5.6 g) was purified by silica gel column chromatography (200–300 mesh, 50 cm × 5 cm, 800 g, petroleum ether-$CHCl_3$, 2:1), further purified by Sephadex LH-20 ($CHCl_3$-MeOH, 1:1) to give compound **5** (23.6 mg) and compound **7** (7.3 mg) (Xu et al., 2007).

2.3.1. 9β-hydroxy-1βH,11αH-guaia-4,10(14)-dien-12,8α-olide (*1*)

Colorless oil. $[\alpha]_D^{20}$=−18 (c = 0.011, $CHCl_3$). IR (KBr): 3435, 1740, 1659, 1071, 931 cm^{-1}. ^{1}H and ^{13}C NMR: see Table 1. HRESIMS: 249.1489 ($[M+H]^+$, $C_{15}H_{21}O_3^+$; 249.1485).

2.3.2. 9β-hydroxy-1βH,11βH-guaia-4,10(14)-dien-12,8α-olide (*2*)

Colorless oil. $[\alpha]_D^{20}$=−33 (c = 0.017, $CHCl_3$). IR (KBr): 3437, 1740, 1658, 1072, 931 cm^{-1}. ^{1}H and ^{13}C NMR: see Table 1. HRESIMS: 249.1488 ($[M+H]^+$, $C_{15}H_{21}O_3^+$; 249.1485).

2.4. Bioassay

The insect species used were *P. xylostella* and *B. odoriphaga*, both of which were used as model of insect pest by us. Meanwhile, the