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Structure-activity relationships of cinnamaldehyde and eugenol derivatives against plant pathogenic fungi

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ABSTRACT

Rhizoctonia solani and *Fusarium oxysporum* are very well known phytopathogens with worldwide spread that cause one of the most destructive diseases, resulting significant yield losses in crop production. In order to find effective fungicides for controlling phytopathogen, the structure-activity relationships of cinnamaldehyde and eugenol derivatives against *R. solani* and *F. oxysporum* were evaluated. Additionally, the composition and fungicidal activity of *Cinnamomum cassia* and *Syzygium aromatica* essential oils was assessed. Cinnamaldehyde (49.75%) is the major compound in cinnamon bark oil, and eugenol (89.17%) is most abundant in clove bud oil. The clove bud oil exhibited good antifungal activities against *R. solani* and *F. oxysporum* (IC_{50} = 106.5 and 149.9 μg/mL, respectively). Cinnamon bark oil showed a lower activity than clove bud oil. The fungicidal activity of cinnamaldehyde (IC_{50} = 75.4 and 156.9 μg/mL, respectively) and eugenol (IC_{50} = 58.9 and 52.9 μg/mL, respectively) against *R. solani* and *F. oxysporum* was also evalutated. Comparisons of the antifungal activities of cinnamaldehyde and eugenol derivatives revealed that α-methylcinnamaldehyde, α-methylcinnamic acid, methyleugenol, acetyleugenol, isoeugenol, methylisoeugenol, and acetylisoeugenol showed good antifungal activities against *R. solani* and *F. oxysporum*. In structure-activity relationships, the fungicidal activity of cinnamaldehyde derivatives could be related to conjugated double bond and the length of CH chain outside the ring. In addition, the presence of the lipophilicity may have a considerable influence on the toxicity of phenylpropenes. The present approach may help future work in the search for fungicidal compounds.

1. Introduction

Pathogenic fungi are one of the major economic problems of crop and food production. *Rhizoctonia solani* and *Fusarium oxysporum* are very well known phytopathogens with worldwide spread, resulting significant yield losses in crop production (Bajpai et al., 2004; Jasso de Rodríguez et al., 2015). *R. solani* is an important necrotrophic pathogen, with a broad host range in crop plants (Nikraftar et al., 2013). The pathogen infects the below ground plant parts and also capable of infecting the above ground plant parts (Bajpai et al., 2004). The plant pathogen *F. oxysporum* is a soil-inhabiting fungus that induces vascular wilt and root rot in a variety of plants by colonizing xylem tissue (Ma et al., 2013; Li et al., 2015). In general, the control of *R. solani* and *F. oxysporum* is usually accomplished by using synthetic fungicides. However, the increasing drug resistance and the environmental safety resulting from antifungal drugs had been reported (Deising et al., 2008; Ramaiah and Garampalli, 2015). Therefore, the need for new antifungal substances and/or an alternative method is becoming increasingly obvious. In recent years, the increasing interest in naturally occurring toxicants from plants is considered as an alternative to synthetic fungicides, due to its less negative effects on human health and environmental safety (Jasso de Rodríguez et al., 2006, 2015). Many works have proven the plant extracts and essential oils may be as alternative sources of antifungal agents (Jasso de Rodríguez et al., 2005, 2007, 2015; Bajpai et al., 2008; Chang et al., 2008; Kordali et al., 2008; Zabka et al., 2009; Cordova-Albores et al., 2014; Khaledi et al., 2015; Rongai et al., 2015).

In traditional Chinese medicine, cinnamon bark (*Cinnamomum cassia* (L.) C. Presl) and clove bud (*Syzygium aromatica* L., *syn. Eugenia caryophyllata* L.) have long been considered to have medicinal properties, such as a stimulant against digestive disorders and diarrhea (Kim et al., 2003; Chen et al., 2014). Meanwhile, they have been used as flavoring agents in foods, beverages, chewing gums, cosmetics etc (Jirovetz et al., 2006; Chen et al., 2014). Previous studies demonstrated that essential oils of cinnamon bark (Salmeron

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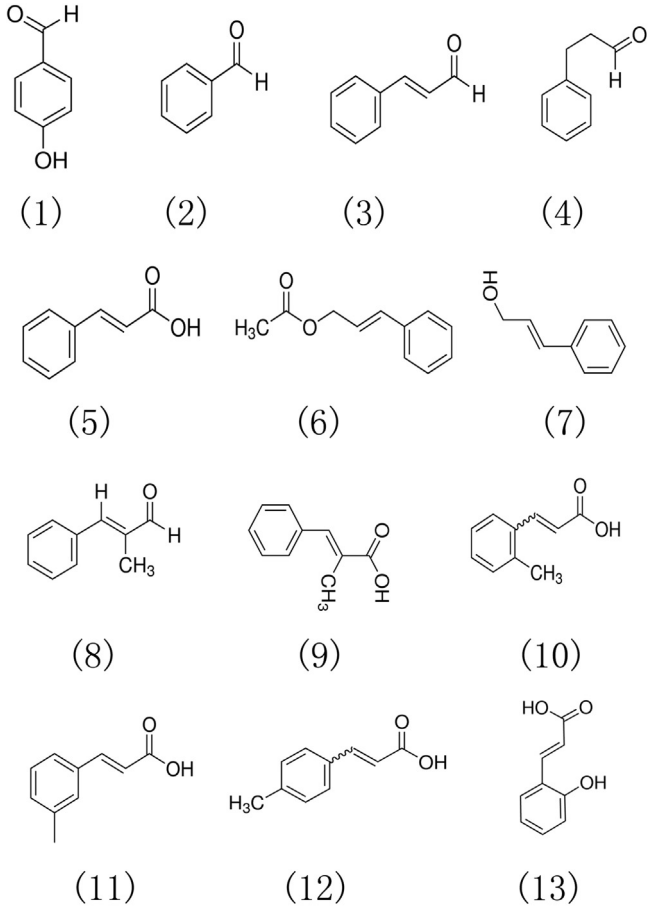

Fig. 1. Structure of test compounds: 1, 4-Hydroxybenzaldehyde; 2, Benzaldehyde; 3, trans-Cinnamaldehyde; 4, 3-Phenylpropionaldehyde; 5, trans-Cinnamic Acid; 6, Cinnamyl Acetate; 7, Cinnamyl Alcohol; 8, α-Methylcinnamaldehyde; 9, α-Methylcinnamic Acid; 10, 2-Methylcinnamic Acid;11, 3-Methylcinnamic Acid; 12, 4-Methylcinnamic Acid; 13, trans-2-Hydroxycinnamic Acid.

and Pozo, 1991; Sinha et al., 1993; Wang et al., 2005; Cheng et al., 2006) and clove bud (Gayoso et al., 2005; López et al., 2005; Chaieb et al., 2007a; Omidbeygi et al., 2007; Viuda-Martos et al., 2007; Pinto et al., 2009; Xing et al., 2012; Xie et al., 2015) possessed antifungal activities against food-borne fungus and white-rot fungus. In addition, previous phytochemical studies disclosed that the major compounds in cinnamon bark and clove bud oils were cinnamaldehyde and eugenol respectively, and the two compounds were found to possess antifungal activities against white-rot fungus (Wang et al., 2005; Cheng et al., 2006; Xie et al., 2015), and food-relevant fungi (Abbaszadeh et al., 2014; Shreaz et al., 2016). However, to the best of our knowledge, anti-phytopathogen activities of cinnamon bark and clove bud and its main compounds have not previously been reported.

Hence, the chemical composition of cinnamon bark and clove bud essential oils, and their anti-phytopathogen activities were investigated. Furthermore, the anti-phytopathogen activity of cinnamaldehyde and eugenol derivatives was also examined to explain the effects of chemical structure on the anti-phytopathogen property.

2. Materials and methods

2.1. Chemicals

All test compounds were of 95% purity or greater, they were purchased from TCI (Shanghai, China). The structures of these compounds are shown in Figs. 1 and 2. Tebuconazole was as the positive control insecticide and purchased from Bayer CropScience (China) Co., Ltd.

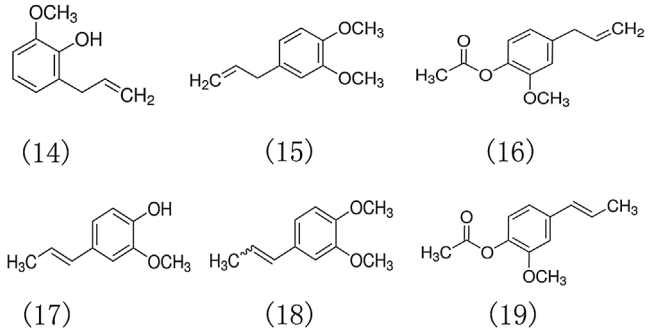

Fig. 2. Structure of test compounds: 14, Eugenol; 15, Methyleugenol; 16, Acetyleugenol; 17, Isoeugenol; 18, Methylisoeugenol; 19, Acetylisoeugenol.

2.2. Fungal strains

The pathogenic fungi were obtained from the Agricultural Culture Collection of China (ACCC). The fungal strains used in experiments were as follows: *Rhizoctonia solani* (ACCC 36124) and *Fusarium oxysporum* (ACCC 37438).

2.3. Essential oil distillation

Cinnamon bark and clove buds were purchased from the local spice store, and identified by Dr. Xue Gong (College of Life Sciences & Technology, Huazhong Agricultural University). The samples (50 g) were subjected to hydrodistillation using a modified Clevenger type apparatus for 6 h (Xie et al., 2011). The obtained distillate was extracted twice with petroleum ether, and the solvent was concentrated in a rotary evaporator under vacuum. The essential oils were stored in sealed vial at −20 °C until use.

2.4. Gas chromatography–mass spectrometry (GC–MS)

The GC–MS analysis was performed on a gas chromatograph Agilent 6890A interfaced with an Agilent 5975C mass spectrometer. A HP-5 MS (cross-linked 5% phenyl methyl silox) capillary column (30 m × 0.25 mm, 0.25 μm film thickness) was used. The column temperature was programmed to rise from 50 to 250 °C at a rate of 10 °C/min. The carrier gas was helium with a flow rate of 1 ml/min. MS were taken at 70 eV and a mass range of 15–500. Identification of compounds of the essential oil was based on retention indices relative to *n*-alkanes and computer matching with the NIST11.LIB (National Institute of Standards and Technology) as well as by comparison of the fragmentation patterns of the mass spectra with those reported in the literatures (Adams, 1995).

2.5. Antifungal assays

The method of Chang et al. (1999) was employed in 9 cm petri dishes, dissolving 200, 150, 100, and 50 μg/mL of essential oil and compounds were added to sterilized potato dextrose agar (PDA) in Petri dishes. After transferring the mycelium of two fungi strains, the test dishes were incubated at 26 ± 1 °C for 3–7 d, until the fungal mycelia growth in the control plates reached the edges of plates. Each test was repeated three times, and the data averaged. The antifungal index was calculated as follows: Antifungal index (%) = (1 - D_a/D_b) × 100 where, D_a = the diameter of growth zone in the experimental plate (cm), D_b = the diameter of growth zone in the control plate (cm).