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Toxicity of quinones against two-spotted spider mite and three species of aphids in laboratory and greenhouse conditions

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ABSTRACT

Toxicities of the eight quinones were evaluated through leaf dip bioassays conducted against *Tetranychus urticae*, *Myzus persicae*, *Myzocallis walshii*, and *Illinoia liriodendri*. Based on LC_{50} values, plumbagin (LC_{50} = 0.001%) was the most active compound against *T. urticae* and ubiquinone Q_0 (LC_{50} = 0.005%), plumbagin (LC_{50} = 0.010%), and dibromothymoquinone (LC_{50} = 0.012%) were the most active compounds against *M. persicae*. The most active compounds against *M. walshii* were juglone (LC_{50} = 0.011%) and ubiquinone Q_0 (LC_{50} = 0.019%), whereas dibromothymoquinone (LC_{50} = 0.030%), plumbagin (LC_{50} = 0.033%) and ubiquinone Q_0 (LC_{50} = 0.058%) were the most toxic to *I. liriodendri*. Ecotrol (positive control) was the least toxic compound (LC_{50} = 0.39%) against *T. urticae* and *M. persicae* (LC_{50} = 0.447%). Although the majority of the compounds tested were toxic to all four test species in residual bioassays, there was little overlap among the test species in terms of susceptibility to the compounds and interspecific differences were observed. Regarding structure–activity relationships for quinones, the addition of a hydroxyl group resulted in a significant increase in the toxicity of the 1,4-naphthoquinones, and those possessing a methyl group exhibited the highest levels of activity in *T. urticae*. The bromine atom at the 2- and 5-positions of the benzoquinone ring is crucial to the toxicity of the compounds against *I. liriodendri*. Toxicity was greatly affected not only by the number of hydroxyl groups, but also by their positions in the ring in the case of *M. walshii*. Juglone and plumbagin as residual toxins in the laboratory also reduced the population of two-spotted spider mites compared to EcoTrol™ (positive control) and the negative control in the greenhouse experiment. Some quinones tested may have potential as commercial insecticides and miticides, or alternatively, could serve as lead compounds for the development of more potent crop protection agents.

1. Introduction

Both aphids and mites are pests of a variety of fruits, vegetables and ornamental crops (Horton et al., 2008) worldwide. The two-spotted spider mite, *Tetranychus urticae* Koch, is considered a serious pest of fruits, vegetables and ornamental plants worldwide (Johnson and Lyon, 1991), with more than 1200 species of host plants reported (Zhang, 2003) including 150 economically important species. Spider mites account for as much as a 5% loss in total agricultural productivity worldwide. Populations of mites tend to explode during periods of low humidity and high temperatures resulting in stippling, lower leaf drop and death of the entire plant (Baker, 1994). Spider mites are also considered one of the most important pests of greenhouse production worldwide in terms of damage and control. Spider mites have evolved resistance to more than 80 acaricides to date in over 60 countries (Jeon et al., 2010).

Reduced growth, wilting, curling, yellowing of foliage and stunting of shoots may result from large aphid populations (van Emden and Harrington, 2007). Additional major problems associated with aphids are their sticky excretions and their ability to transmit viruses (Kaliciak and Syller, 2009). The green peach aphid, *Myzus persicae* (Hemiptera: Aphididae), is a cosmopolitan species that has developed resistance to numerous synthetic insecticides (Kim et al., 2009). The green peach aphid is a generalist species feeding on hundreds of host plants in more than 40 plant families (Leonard et al., 1970). The oak tree (*Quercus*) aphid, *Myzocallis walshii* and the tulip tree (*Liriodendron tulipifera*) aphid, *Illinoia liriodendri* are specialist species constituting the foremost urban tree pests in the western United States, as well as in other parts of the world. The

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honeydew excreted by *M. walshii* and *I. liriodendri* cause aesthetic damage to trees and public disturbance (Pons et al., 2006). The honeydew leaves a sticky residue on parked cars and side-walks, but also provides an excellent medium for the growth of a black “sooty mold”, further reducing the aesthetic appearance of trees. Black mold can decrease light penetration, and thereby, reduces tree growth. Although aphids seldom kill a mature plant, the damage and unsightly honeydew they generate sometimes warrants control.

Many insects confirmed to be resistant to synthetic pesticides have continued to grow, a problem that compounds the risks associated with their use (Ahn et al., 1998; Park et al., 2000). The effective insecticides available to date can pose a significant risk to human health and environmental safety if improperly utilized, and may kill natural enemies causing target pest populations to rise above untreated levels (Lim et al., 2008). Thus, there is a need to develop reduced-risk alternatives to synthetic pesticides. Plant extracts and phytochemicals have long been a subject of research in an effort to develop alternatives to conventional insecticides causing minimal effects on the environment and non-target organisms. Many of these phytochemicals are thought to provide natural defense against herbivores and pathogens to the plants that produce them.

These putatively defensive phytochemicals include terpenoids, flavonoids, quinones, and alkaloids (Park et al., 2011). Among these classes, many quinones are widely distributed in nature and encompass the functional constituents of several biochemical systems (Lee et al., 2010). More than 2000 naturally occurring quinones, particularly derivatives of benzoquinone and naphthoquinone, have been isolated from lower and higher plant species (Lee and Lee, 2006, 2008). Moreover, the quinoid structure in various quinone derivatives – both natural and synthetic – has been shown to exhibit a wide range of interesting biological activities including antibacterial, antibiotic, antimalarial, antitumor, antiviral, fungicidal, and herbicidal effects (Weissenberg et al., 1997). Recently, natural quinones and some derivatives have attracted attention as insecticidal and/or antifeedant compounds (Burgueno-Tapia et al., 2008). In particular, certain 1,4-naphtho- and 1,4-benzoquinone structures are associated with acaricidal, antifeedant and insecticidal activities (Norris, 1986; Lee, 2009). However, only a small group of quinones have been tested to date for these biological activities (Motti et al., 2007). The main objective of the present study was to evaluate the toxicity of some naturally occurring quinones and some easily synthesized quinone derivatives on the two-spotted spider mite and three aphid species.

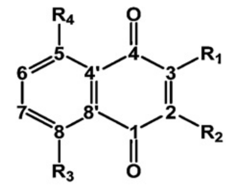
2. Materials and methods

2.1. Mites and aphids

Colonies of *T. urticae* were reared on green bush bean (*Phaseolus vulgaris* L. cv. Speculator #24A Stokes) plants inside a growth chamber at 24 ± 3 °C and 50–60% relative humidity (RH) under a 16:8 LD photoperiod. *M. persicae* were reared on pakchoy (*Brassica chinensis*), *M. walshii* on oak leaves (*Quercus rubra*) and *Illinoia liriodendra* on tulip leaves (*Liriodendron tulipifera*) in the lab at a temperature of 25 ± 1 °C and under a 16:8 LD photoperiod. Oak leaves and tulip leaves, along with the aphids, were collected from respective trees growing on the University of British Columbia campus (Vancouver, Canada), and maintained in the laboratory until use.

2.2. Plant material

Bean plants were grown in the horticulture greenhouse at the University of British Columbia at 24 ± 3 °C and 45–60% relative humidity (RH) under natural daylight. The plants were watered three times per week, twice with water and once with water-soluble fertilizer (Peters EXCEL 15-5-15 Cal-Mag, The Scotts Co., Marysville, OH).



Compounds	R_1	R_2	R_3	R_4
1,4-Naphthoquinone (NQ)	H	H	H	H
Juglone (5-Hydroxy-1,4-NQ)	H	H	H	OH
Naphthazarin (5,8-Dihydroxy-1,4-NQ)	H	H	OH	OH
Plumbagin (5-Hydroxy-2-methyl-1,4-NQ)	H	CH_3	H	OH
Dichlon (2,3-Dichloro-1,4-NQ)	Cl	Cl	H	H

Fig. 1. Chemical structures of the five 1,4-naphthoquinones used in this study.

2.3. Chemicals

Juglone (5-hydroxy-1,4-naphthoquinone), plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) and thymoquinone (6-isopropyl-3-methyl-1,4-benzoquinone) were isolated from *Caesalpinia sappan* heartwoods, *Diospyros kaki* roots and *Nigella sativa* seeds, respectively (Lee and Lee, 2006, 2008; Lee, 2009). Dichlon (2,3-dichloro-1,4-naphthoquinone), naphthazarin (5,8-dihydroxy-1,4-naphthoquinone), 1,4-naphthoquinone, dibromothymoquinone (2,5-dibromo-6-isopropyl-3-methyl-1,4-benzoquinone) and ubiquinone Q_0 (2,3-dimethoxy-5-methyl-1,4-benzoquinone) were purchased from Aldrich (Milwaukee, WI) and Sigma (St. Louis, MO). The structures of these compounds are shown in Figs. 1 and 2. EcoTrol™ was provided by EcoSMART Technologies Inc. (Franklin, TN, USA). All other chemicals were of analytical grade and commercially available.

2.4. Leaf dip bioassay

Leaf-dip bioassays were conducted to determine the residual effects of the compounds. Leaf discs ($3.8\,cm^2$) cut from *Brassica chinensis* (Brassicaceae), *Liliodendron tulipfera* (Magnoliaceae), *Quercus rubra* (Fagiaceae), and *Phaseolus vulgaris* (Fabaceae) were dipped in solutions of test compounds for 10 s for the bioassays with green peach aphid, oak aphids, tulip tree aphids (third-fourth instar) and adult spider mites. Methanol or methanol:dichloromethane (2:1) was utilized as a carrier solvent. Each small beaker contained 400 μL of solution, with each leaf disc receiving >100 μL

of the solution. After dipping, discs were air-dried in glass Petri dishes (90 mm × 15 mm) at room temperature. After drying, each leaf disc was placed individually in a Petri dish (50 mm × 9 mm). Ten aphids or mites were introduced onto the leaf disc and covered with a lid. Mortality was determined after 48 h.