CAFFEYLTARTRONIC ACID FROM CATNIP (Nepeta cataria): A PRECURSOR FOR CATECHOL IN LUBBER GRASSHOPPER (Romalea guttata) DEFENSIVE SECRETIONS

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Abstract—Adults of the lubber grasshopper (Romalea guttata) secrete increased amounts of catechol from their defensive glands when fed diets containing only catnip leaves (Nepeta cataria). Model compound bioassays showed that these insects were able to sequester and biomagnify simple phenols, such as catechol and hydroquinone, in their defense gland secretions. Excessive catechol secretions from caffeic acid-fortified diets indicated met-

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ABOLIC pathways exist to perform efficiently more complex biochemical conversions. Reverse-phase HPLC of methanol extracts of catnip revealed only one major caffeoyl-polyphenol as a possible precursor for the observed elevated catechol secretions, when this plant is fed to lubbers. The compound was shown to be caffeoyltartronic acid (CTA). During analysis of CTA by probe-MS or gas chromatography (of its silylated derivative), CTA decomposed by loss of carbon dioxide to form caffeoylglycolic acid (CGA), making identification by these methods ambiguous. Only fast atom bombardment mass spectrometry (FAB-MS, negative mode) gave a true molecular weight. Ground-ivy (*Glecoma hederacea*), a relative of catnip, was also shown to contain CTA. The mung bean (*Phaseolus radiatus = Vigna radiata*), a species totally unrelated to catnip, is the only other reported plant source of CTA. Catnip leaves were found to contain about twice as much CTA as mung bean leaves.

**Key Words**—Catnip, *Nepeta cataria*, caffeoyltartronic acid, lubber grasshopper, *Romalea guttata*, catechol secretions.

**INTRODUCTION**

Many insects sequester plant allelochemicals, and these compounds often constitute key elements in the chemical arsenals of these herbivores (Rothschild, 1972; Blum, 1981). Plant natural products or their metabolites are frequently incorporated into the defensive secretions of insects (Duffey, 1980; Jones et al., 1989; Blum et al., 1987, 1990) but, for the most part, the metabolic pathways for these altered plant constituents are unknown. Recent investigations on the chemistry of the deterrent exudate produced in the metathoracic glands of a generalist herbivore, the lubber grasshopper (*Romalea guttata*), demonstrate that while some compounds in this secretion may be biotransformed from obvious precursors, the origins of others do not appear to be as readily apparent (Blum et al., 1990). Notwithstanding the metabolic eclecticism that characterizes these phytochemicals, it is evident that the deterrent value of the secretions (towards ants; Blum et al., 1990) may reflect both the quantitative and qualitative properties of selected plant compounds.

*R. guttata* is an excellent model for studying the chemistry of plant-derived defensive secretions because these grasshoppers discard the glands, plus their secretions, when they molt. These insects, with their new, empty glands, can be fed either selected plant species or candidate compounds. Indeed, the chemistry of the subsequent secretions reflects the ingested allelochemicals that have been sequestered and/or metabolized before or after storage in the defensive glands (Jones et al., 1987; Blum et al., 1990).

The concentrations of catechol and hydroquinone, two major glandular constituents, are subject to great perturbations when grasshoppers are fed on different diets. For example, concentrations of these two phenolics in defensive gland secretions were depressed when lubbers were fed only lettuce or an arti-