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PEST MANAGEMENT

Insecticidal Activity of Piper Essential Oils from the Amazon Against the Fire Ant *Solenopsis saevissima* (Smith) (Hymenoptera: Formicidae)

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Abstract

Pepper plants in the genus *Piper* (Piperales: Piperaceae) are common in the Brazilian Amazon and many produce compounds with biological activity against insect pests. We evaluated the insecticidal effect of essential oils from *Piper aduncum*, *Piper marginatum* (chemotypes A and B), *Piper divaricatum* and *Piper callosum* against workers of the fire ant *Solenopsis saevissima* (Smith) (Hymenoptera: Formicidae), as well as their chemical composition by gas chromatography and gas chromatography–mass spectrometry. The lowest median lethal concentration (LC$_{50}$) in 48 h was obtained with the oil of *P. aduncum* (58.4 mg/L), followed by the oils of *P. marginatum* types A (122.4 mg/L) and B (167.0 mg/L), *P. divaricatum* (301.7 mg/L), and *P. callosum* (312.6 mg/L). The major chemical constituents were dillapiole (64.4%) in the oil of *P. aduncum*; *p*-mentha-1(7),8-diene (39.0%), 3,4-methylenedioxypropiophenone (19.0%), and (*E*)-β-ocimene (9.8%) in *P. marginatum* chemotype A and (*E*)-isoosmorhizole (32.2%), (*E*)-anethole (26.4%), isoosmorhizole (11.2%), and (*Z*)-anethole (6.0%) in *P. marginatum* chemotype B; methyleugenol (69.2%) and eugenol (16.2%) in *P. divaricatum*; and safrole (69.2%), methyleugenol (8.6%), and β-pinene (6.2%) in *P. callosum*. These chemical constituents have been previously known to possess insecticidal properties.

Introduction

The growing interest in insecticides of plant origin is motivated by the need to reduce the negative environmental and health impacts of pesticides and to deal with the challenge of pesticide resistance. Several studies have been conducted using plant products with the aim of broadening the knowledge on their insecticide, repellent, and growth, breeding and feeding inhibitory properties to a variety of insects. Essential oils and their constituents have been shown to be potentially active as insecticides. Terpenoid and phenylpropanoid compounds that occur in these oils are responsible for most of the repellent, insecticidal, and toxic activities reported so far. Terpenic oils from a variety of plants have shown quite active against a number of insects, including ant species (Ellis & Bradley 1996, Meissner & Silverman 2001, Appel *et al* 2004).

Phenylpropanoids, particularly safrole, isosafrole, eugenol, isoeugenol, and/or methyleugenol, among others, were shown to be toxic and/or repellent to species belonging to different orders of insects (Ngoh *et al* 1998, Huang *et al* 2002, Yang *et al* 2003). Dillapiole has also showed *in vitro* synergism with pirethroids and carbamates, besides displaying its own insecticidal properties (Lichtenstein *et al* 1974, Tomar *et al* 1979a, b, Bernard *et al* 1990, Almeida *et al* 2009).

A significant cercaricidal activity against *Schistosoma mansoni* (Platyhelminthes: Trematoda) has been detected for the oil of *Piper marginatum* (Frischkorn *et al* 1978), an oil which later we report the chemical composition of some chemotypes (Andrade *et al* 2008).

The family Piperaceae comprises five genera with nearly 1,400 species with a mainly pan tropical distribution (Jaramillo & Manos 2001). The family is represented by herbs, lianas, shrubs and rarely by trees. *Piper* is the largest genus in the family with about 1,000 species, amongst them there are about 170 species occurring in Brazil (Yuncker 1972). *Piper* from the Brazilian Amazon has yielded essential oils rich in terpenoids and phenylpropanoids (Maia *et al* 1987, Andrade *et al* 1998, 2008, Santos *et al* 1998, Luz *et al* 2000, 2003). The oils of *Piper hispidinervum* and *Piper callosum*, both rich in safrole, can be used as raw materials in obtaining piperonyl butoxide, a synergist agent that stabilizes and potentiates the insecticidal action of natural pyrethroids (Maia *et al* 1993). The oil of *Piper aduncum*, rich in dillapiole, showed fungicidal activity against *Crinipellis perniciosa* (Agaricales: Tricholomataceae), the fungus known as the “witches’ broom” which reduces the productivity of cocoa in the Amazon, as well insecticidal activity against the mosquitoes *Anopheles marajoara* Galvão & Damasceno and *Aedes aegypti* (L.) (Diptera: Culicidae), vectors of malaria and dengue (Maia *et al* 1998, Almeida *et al* 2009).

Solenopsis saevissima (F Smith) (Hymenoptera: Formicidae) has its origin in South America and occurs from the Galapagos Islands to Chile. It is abundant in the Amazon Basin along the river banks and in open grassy areas. In urbanized areas, this species has caused serious problems in Northern Brazil and it is also one of the most frequent species occurring in urbanized areas in Southern and Southeastern Brazil. This fire ant species can inflict serious injuries to people and cause major economic damage in forestry land (Lofgren 1986, Williams 1994).

Therefore, we aimed to determine the insecticidal activity of the essential oils of *P. aduncum*, *P. marginatum* (chemotypes A and B), *Piper divaricatum* and *P. callosum* against worker ants of *S. saevissima*, as well as to report on the chemical composition of these oils.

Material and Methods

Insect material

Workers of *S. saevissima* used in the bioassays were collected from fragments of colonies existing at the Centro de Pesquisas Zoobotânicas e Geológicas, Instituto de Pesquisa Científicas e Tecnológicas do Estado do Amapá (IEPA), Macapá, Amapá, Brazil (00°02′17″ S, 51°05′37″ W) and kept in the laboratory using the same technique applied by Banks *et al* (1981).

Plant material and processing

The species of *Piper* were collected in different localities of the Amazon region, Brazil, during the rainy season (Table 1). The plants were identified by Dr. Elsie Guimarães, a Piperaceae specialist from the Jardim Botânico do Rio de Janeiro, RJ, Brazil. Specimens were deposited in the herbarium of the Museu Emilio Goeldi, in Belém, PA, Brazil.

The aerial parts of the plants were air-dried, ground and subjected to hydrodistillation using a Clevenger-type apparatus (100 g for 3 h). The oils were dried over anhydrous sodium sulfate and its percentage contents were calculated on the basis of the plant dry weight. The moisture content of the samples were calculated after phase separation in a Dean–Stark trap (5 g for 1 h), using toluene.

Oil-composition analysis

The analysis of the oil was carried out on a THERMO DSQ II GC-MS instrument, under the following conditions: DB-5ms (30 m×0.25 mm; 0.25 μm film thickness) fused-silica

Table 1 Data collection for the *Piper* species assayed against *Solenopsis saevissima*.

Species	Plant part	Collection site	Coordinates	Oil (%)
Piper aduncum	Leaves and fine stems	Perimetral Avenue, Campus NPI, Belém, PA, Brazil	01°27′21″ S 48°30′16″ W	1.2
Piper divaricatum	Leaves and fine stems	Bagre Avenue, Breves, PA, Brazil	01°40′56″ S 50°28′49″ W	1.5
Piper marginatum (chemotype A)	Leaves and fine stems	Augusto Montenegro Road, city of Belém, PA, Brazil	01°27′21″ S 48°30′16″ W	0.4
Piper marginatum (chemotype B)	Leaves and fine stems	Park 10, Manaus, AM, Brazil	03°06′07″ S 60°01′30″ W	1.4
Piper callosum	Leaves and fine stems	ERJOH/CEPLAC area, Marituba, PA, Brazil	01°21′19″ S 48°20′31″ W	3.6

Table 2 Volatile constituents (in percent) identified in the oils of *Piper* species.

Constituents	RI[a]	*Piper aduncum*	*Piper marginatum*		*Piper divaricatum*	*Piper callosum*
			Type A	Type B		
α-pinene	934	1.2	1.7	0.1	1.2	1.5
Camphene	948		0.9	0.1		0.2
Sabinene	970	tr		0.2	0.1	0.3
β-pinene	978	1.5	0.7		1.2	6.2
Myrcene	990	0.4	0.5		0.2	0.3
α-phellandrene	1,003	0.4		0.2	tr	tr
p-mentha-1(7),8-diene	1,004	0.4	39.0	1.0		
α-terpinene	1,014	0.3				
p-cymene	1,025	0.2				0.3
Limonene	1,026	1.1	0.4	0.3	0.3	1.6
β-phellandrene	1,027	tr			0.5	
(*Z*)-β-ocimene	1,035	1.5	4.7		0.1	
(*E*)-β-ocimene	1,045	3.0	9.8		2.3	
γ-terpinene	1,056	0.9	0.1			
Terpinolene	1,088	2.0	0.2			
Linalool	1,095	0.1	0.4			0.3
Camphor	1,146		0.2	0.5		0.1
Isoborneol	1,155					0.1
Borneol	1,165			0.5		
4-terpineol	1,174	1.2				tr
p-cymen-8-ol	1,181	0.2				
α-terpineol	1,187					0.1
Methylchavicol	1,197		0.2	0.5		
Piperitone	1,251	3.3				
(*Z*)-anethole	1,252			6.0		
(*E*)-anethole	1,284			26.4		
Safrole	1,288		3.4		2.5	69.2
Bornyl acetate	1,289			0.1		
δ-elemene	1,335		0.2		tr	
eugenol	1,357				16.2	
Cyclosativene	1,370	0.3				
α-copaene	1,376	1.0	0.4	1.4		0.4
β-cubebene	1,385					0.1
β-bourbonene	1,388		0.2			
β-elemene	1,390	0.3	0.3	1.0	0.3	
Methyleugenol	1,403		1.7		69.2	8.6
(*E*)-caryophyllene	1,416	2.5	2.9	2.6		0.4
β-gurjunene	1,432	0.2			0.1	
α-humulene	1,455	0.8		0.4	0.1	0.1
isoosmorhizole	1,466			11.2		
γ-muurolene	1,479					0.4
Germacrene D	1,484	2.7	1.8		3.5	0.8
β-selinene	1,489		0.3	3.6		
(*E*)-methylisoeugenol	1,491				0.1	0.2
α-selinene	1,498			0.7		
Bicyclogermacrene	1,500	2.0			0.2	
α-muurolene	1,501			0.3		

Table 2 (continued)

Constituents	RI^a	*Piper aduncum*	*Piper marginatum*		*Piper divaricatum*	*Piper callosum*
			Type A	Type B		
(*E*,*E*)-α-farnesene	1,505	0.2				
Germacrene A	1,508			0.2	0.2	
γ-cadinene	1,513				tr	
Cubebol	1,515					0.3
(*E*)-isoosmorhizole	1,517			32.2		
Myristicin	1,519	0.5	2.7			
Eugenol acetate	1,522				0.9	
δ-cadinene	1,523	0.4			0.1	0.2
3,4-methylenedioxypropiophenone	1,544		19.0			
Elemol	1,549			1.9		0.1
Elemicin	1,555		2.6		0.1	1.9
Germacrene B	1,560	0.4				
(*E*)-nerolidol	1,563				0.1	0.1
Germacrene D-4-ol	1,574					0.6
Spathulenol	1,577	1.3				
Caryophyllene oxide	1,582	0.8		0.2		0.1
Globulol	1,584	0.8				tr
Dillapiole	1,621	64.4				
γ-eudesmol	1,632			1.8		
epi-α-muurolol	1,643					0.1
α-muurolol	1,645					0.4
β-eudesmol	1,651			3.2		0.3
2-hydroxy-4,5-methylenedioxypropiophenone	1,642		1.6			
α-cadinol	1,654					0.2
2-methoxy-4,5-methylenedioxypropiophenone	1,713			1.1		
Monoterpene hydrocarbons		12.9	58.0	1.9	5.9	10.4
Oxigenated monoterpenes		4.8	0.8	1.0	–	0.6
Sesquiterpene hydrocarbons		10.8	7.8	10.3	4.5	2.5
Oxigenated sesquiterpenes		2.9	–	7.1	0.1	2.1
Phenylpropanoids		64.9	29.3	74.4	89.0	79.9
Total		96.3	95.9	97.7	99.5	95.5

RI retention time on DB-5ms column, *tr* traces.

capillary column; programmed temperature: 60–240°C (3°C/min); injector temperature: 250°C; helium was used as carrier gas at 32 cm/s (measured at 100°C); injection type: splitless (2 μL of a 1:1,000 hexane solution); split flow was adjusted to yield a 20:1 ratio; septum sweep was constant at 10 ml/min; EIMS: electron energy, 70 eV; temperature of ion source and connection parts: 200°C. The quantitative data regarding the volatile constituents were obtained by peak-area normalization using a FOCUS GC/FID operated under the same conditions of GC-MS, except for the carrier gas which was nitrogen. The retention index was calculated for all the volatiles constituents using an *n*-alkane (C_8–C_{40}, Sigma-Aldrich) homologous series.

Individual components were identified by comparison of both mass spectrum and GC retention data with authentic compounds which were previously analyzed and stored in the data system, as well as with the aid of commercial libraries containing retention indices and mass spectra of volatile compounds commonly found in essential oils (NIST 2005, Adams 2007).

Bioassays

The bioassays were conducted at the Laboratório de Entomologia, Centro de Pesquisas Zoobotânicas e Geológicas, IEPA, Macapá, Amapá, Brazil, under controlled

Table 3 Mean mortality (in percent) of fire ants caused by different concentrations of *Piper* oils (Tukey's test, $P<0.05$).

Oils	Concentrations (mg/L)										Control
	24 h					48 h					
	100	200	300	400	500	100	200	300	400	500	
Piper aduncum	50.6±2.7a	53.8±3.3a	66.1±5.2a	77.6±4.5a	78.6±4.5a	68.9±3.1a	78.6±4.8a	81.9±5.3a	84.4±3.6a	100.0±0.0a	0
Piper marginatum chemotype A	40.9±3.6b	43.6±3.0b	60.5±4.3b	76.7±4.1a	77.6±3.5a	57.1±4.4b	60.4±3.6b	70.6±4.8b	84.4±3.2a	100.0±0.0a	0
P. marginatum chemotype B	30.2±2.8c	33.9±4.5c	40.9±4.4c	47.4±4.5b	59.1±3.5b	55.8±3.6b	55.8±4.4b	67.5±3.3b	81.0±4.7a	100.0±0.0a	0
Piper divaricatum	26.1±3.3c	33.9±4.3c	40.9±6.3c	45.5±3.9b	50.6±4.6c	46.2±4.3c	51.3±3.9c	67.5±5.2b	76.6±3.9b	79.8±3.7b	0
Piper callosum	25.1±4.1c	27.6±3.9d	38.2±5.8d	45.5±4.5b	45.5±3.2c	43.6±3.9c	44.2±4.5d	55.9±3.9c	62.4±4.3c	70.6±3.6c	0

Means followed by different letters in the same column differ by Tukey's test ($P<0.05$); each treatment had five replicates ($n=600$).

conditions (25±2°C, 75±5% RH, 12 h photophase). The selection of oil concentrations was based on a series of preliminary tests using the technique of contact to a contaminated surface (paper filter) to obtain the range of responses, i.e., in the concentration ranges of the oils that cause insect mortality, varying from near zero to near 100%. The concentration-mortality tests were conducted after placing the ants within Petri dishes (150×20 mm) containing a filter paper (150 mm diameter) at the bottom impregnated with 1.0 mL of oil solution in acetone, at 100, 200, 300, 400, and 500 mg/L. Acetone was used as control. From each oil concentration (and control) five replicates were conducted, each one with 20 ants (different sizes), totalizing 3,000 ants in all treatments. The filter paper was previously dried by air for 30 min before being placed within the Petri dishes. Dishes also had their lateral surface coated with Teflon to force the ants to remain in contact with the treated surface and to prevent them from escaping. Ant mortality was assessed after 24 and 48 h of the beginning of the experiment (Anonymous 1974). Ant mortality (in percent) was assessed as follows: $\text{Mortality}(\%) = \text{number of dead ants in control} - \text{number of dead ants in treatment}/\text{number of dead ants in control} \times 100$.

Data on ant mortality were transformed into arc sin $\sqrt{x}$ and subjected to analysis of variance and whenever differences were observed, the averages obtained were compared by the Tukey's test ($P\leq0.05$). The statistical program used was the NTIA, version 4.2.1, developed by Embrapa, Campinas, São Paulo, Brazil. The lethal concentrations (LC_{50}, LC_{90}, and LC_{95}), the usual parameters in the measure of the effectiveness of insecticidal molecules, were determined using the SPSS software, version 8.0 for Windows (SPSS 2002).

Results and Discussion

The specimens of *P. aduncum*, *P. marginatum* (chemotypes A and B), *P. divaricatum*, and *P. callosum* yielded oils from 0.4% to 3.6% (see Table 1) and its volatile constituents were analyzed by gas chromatography and gas chromatography–mass spectrometry (Table 2). In total, 72 compounds were identified covering more than 95% of the total composition (Table 2). The main constituent in the oil of *P. aduncum* was dillapiole (64.4%); in the oils of *P. marginatum* were *p*-mentha-1(7),8-diene (39.0%), 3,4-methylenedioxypropiophenone (19.0%), and (*E*)-β-ocimene (9.8%) for the chemotype A and (*E*)-isoosmorhizole (32.2%), (*E*)-anethole (26.4%), isoosmorhizole (11.2%), and (*Z*)-anethole (6.0%) for the chemotype B; in the oil of *P. divaricatum* were methyleugenol (69.2%) and eugenol (16.2%); and in the oil of *P. callosum* were safrole (69.2%), methyleugenol (8.6%) and β-pinene (6.2%).

Solenopsis saevissima worker mortality differed significantly within the same oil, among oils, and between oils and control (F=11.7; df=16; P<0.0001). Regarding the exposure time (24 and 48 h) of the insects to the various concentrations of the essential oils of *Piper*, the mean mortality were significantly higher at 48 h (F=23.0; df= 16; P<0.0001) (Table 3).

LC_{50}, LC_{90}, and LC_{95} were estimated for all of the essential oils of *P. aduncum*, *P. divaricatum*, *P. marginatum* (chemotypes A and B), and *P. callosum* tested with confidence intervals of 95% and for both exposure periods (24 and 48 h) (Table 4).

The lethal insecticidal action by each *Piper* essential oil against *S. saevissima* differed significantly (F=49.9; df=4; P<0.0001), with the most active being that of *P. aduncum*, followed by the oils of *P. marginatum* chemotypes A and B, *P. divaricatum*, and *P. callosum* (Table 4).

The toxic activity of the oil of *P. aduncum* has already been observed for some insect pests (Bernard *et al* 1995), but we believe that the higher insecticidal activity of the oil of *P. aduncum* to workers of *S. saevissima* is due to its major compound dillapiole (64.4%), as this molecule is highly active against mosquitoes (Almeida *et al* 2009). Dillapiole has also been reported as a synergist of several natural insecticides, including carbamates and organochlorines, pyrethrum, tenulin, and azadirachtin and may have the same action with other molecules available in the essential oil of this *Piper* species, providing higher stability and insecticidal activity to this oil (Handa & Dewan 1974, Tomar *et al* 1979a, b, Bernard *et al* 1990, Bertrand 1992).

The oils of *P. marginatum* (chemotypes A and B) showed the second highest insecticidal activity against *S. saevissima* in comparison to other species of *Piper*. In the oil of chemotype A, we can assign its toxic action to the high contents of *p*-mentha-1(7),8-diene (39.0%) and 3,4-methylenedioxypropiophenone (19.0%), followed by minor amounts of myristicin, elemicin, and 2-hydroxy-4,5-methylenedioxypropiophenone. The compound *p*-mentha-1(7),8-diene is an isomer of limonene, also known as pseudolimonene. The attributes of limonene and its isomers acting as insecticidal agents is already well known (Karr & Coats 1988, Vogt *et al* 2002). In turn, the compound 3,4-methylenedioxypropiophenone contains the methylenedioxyphenyl group, characteristic of many other compounds derived from secondary metabolism of plants, as dillapiole and safrole occurring in *P. aduncum* and *P. hispidinervum*, respectively, as well as piperine and piperolein existing in *P. nigrum*, traditionally used as botanical insecticides (Mukerjee *et al* 1979, Scott *et al* 2008). For example, the methylenedioxyphenyl group is found in piperonyl butoxide (molecule derived from safrole), a commercial synergist which interacts with the P-450 cytochrome and inhibits the activity of this polysubstrate monooxygenase,

Table 4 Lethal concentrations and confidence intervals (95%) for the *Piper* essential oils acting as insecticide against the fire ant *Solenopsis saevissima* at different exposure periods.

Species	Oil concentration (mg/L)					
	LC_{50} 24 h	LC_{90}	LC_{95}	LC_{50} 48 h	LC_{90}	LC_{95}
Piper aduncum	114.4 (46.1–159.9)	486.1 (430.7–573.6)	591.5 (517,3–713.4)	58.4 (52.4–160.2)	253.4 (206.1–308.4)	358.8 (304.5–455.4)
Piper marginatum chemotype A	207.8 (174.0–235.8)	493.2 (448.2–556.1)	574.1 (518.1–655.6)	122.4 (68.0–124.6)	480.3 (413.7–600.0)	492.5 (517.8–794.5)
P. marginatum chemotype B	419.3 (382.9–467.9)	776.9 (683.1–927.6)	878.2 (765.5–1,060.0)	167.0 (139.4–189.9)	427.0 (391.0–476.7)	534.8 (483.9–606.9)
Piper divaricatum	552.2 (455.5–793.6)	1,302.4 (976.2–1,625.0)	1,515.7 (1,120.0–1,634.0)	301.7 (46.8–339.8)	485.9 (347.7–540.1)	612.5 (416.3–742.9)
Piper callosum	571.1 (414.8–565.8)	1,476.2 (807.2–1,508.0)	1,719.4 (915.0–1,821.0)	312.6 (152.8–456.3)	690.7 (589.7–874.8)	826.3 (695.2–1,068.0)

an enzyme responsible for the metabolism of toxins in the insects (Belzile *et al* 2000). In the oil of chemotype B of *P. marginatum*, it is possible that the toxicity may be due to the phenylpropanoids (*E*)-isoosmorhizole, isoosmorhizole, and (*E*)- and (*Z*)-anethole. With respect to the first two compounds, there is no record of biological activity, but, (*E*)-anethole is highly effective as fumigant against *Blatella germanica* (L.), *Sitophillus oryzae* (L.), *Callosobruchus chinensis* (L.), and *Lasioderma serricorne* (F.) (Kim & Ahn 2001, Chang & Ahn 2002).

The toxicity the oil of *P. divaricatum* against *S. saevissima* may be attributed to methyleugenol (69.2%) and eugenol (16.2%), whose insecticidal properties were previously discussed here (Ngoh *et al* 1998, Huang *et al* 2002, Yang *et al* 2003). As mentioned earlier, this oil showed a lower toxicity than the oils of *P. aduncum* and *P. marginatum*.

The oil of *P. callosum*, the least toxic of all oils tested, is rich in safrole, but our experience has shown that this compound alone does not have significant insecticidal activity, despite the presence of the methylenedioxyphenyl group in its structure. On the other hand, when transformed in piperonyl butoxide, it acts as a synergist of natural insecticides due to the raise of its lipophilicity (Maia *et al* 1993).

It seems that the major volatile components found in the oils of *P. aduncum*, *P. marginatum*, *P. divaricatum*, and *P. hispidinervum* are responsible for the insecticidal activity observed, but further studies are needed to confirm these results. Furthermore, we also think that other future investigations will be important to establish the use of these oils in sustainable pest control programs in the Amazon.

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