SESQUITERPENES OF AMAZONIAN *Piper* SPECIES*

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ABSTRACT — The essential oils from leaves and thin branches of *Piper amapense, Piper duckei* and *Piper bartlingianum* were analysed by GC/MS and all volatile compounds were identified as sesquiterpenes. The main constitutents identified in the oil of *P. amapense* were *trans*-caryophyllene (25.0%), caryophyllene oxide (17.0%) and β-selinene (15.0%). The oil of *P. duckei* was dominated by *trans*-caryophyllene (23.5%), caryophyllene oxide (18.4%), β-eudesmol (9.4%) and α-eudesmol (9.1%). The major components found in the oil of *P. bartlingianum* were α-cadinol (11.2%), β-elemene (10.5%), α-muurolol (9.4%), (E)-nerolidol (9.0%).

Key words: *Piper amapense, Piper duckei, Piper bartlingianum,* Piperaceae, Essential oils, Sesquiterpenes.

Sesquiterpenos de Espécies de *Piper* da Amazônia.

RESUMO — Os óleos essenciais obtidos das folhas e galhos finos de *Piper amapense, Piper duckei* e *Piper bartlingianum* foram analisados por GC/MS. Os óleos dessas espécies são constituídos na sua totalidade por sesquiterpenos. Os principais constituíntes identificados no óleo de *P. amapense* foram *trans*-cariofileno (25,0%), óxido de cariofileno (17,0%) e β-selineno (15,0%). O óleo de *P. duckei* foi dominado por *trans*-cariofileno (23,5%), óxido de cariofileno (18,4%), β-eudesmol (9,4%) e α-eudesmol (9,1%). Os mais importantes componentes encontrados em *P. bartlingianum* foram α-cadinol (11,2%), β-elemene (10,5%), α-muurolol (9,4%), (E)-nerolidol (9,0%).

Palavras-chave: *Piper amapense, Piper duckei, Piper bartlingianum,* Piperaceae, óleos essenciais, sesquiterpenos.

INTRODUCTION

The family Piperaceae comprises 12 genera and about 1400 species of mainly pantropical distribution (Barroso, 1978). *Piper* species are found in all the world's tropical rainforests and are the dominant understory species in many Neotropical forests. The genus contains more than 700 species, of which about 170 grow wild in Brazil (Yuncker, 1972). The medicinal uses of *Piper* species include treatments for venereal diseases, intestinal disorders (Addae-Mensah *et al.*, 1977), genito-urinary-maladies, epilepsy and to prevent conception (Atal *et al.*, 1975). Traditionally they are also used against pests (Bernard *et al.*, 1995). *Piper bartlingianum* is a shrub of wide distribution in northern Brazil, were it is used as fish-poison (Acevedo-Rodríguez, 1990). The amide dihydropiplartine was isolated from its benzene extract (Kijoa *et al.*, 1982). Investigations on the constituents of the volatile oil of these species have not been reported previously. This paper reports the chemical composition of the essential oils of *Piper amapense, Piper duckei* and *Piper bartlingianum.*

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MATERIAL AND METHODS

The leaves and thin branches of the collected *Piper* species were air-dried for seven days and water-distilled for two hours. The oil obtained was dried over anhydrous sodium sulphate and the yield was calculated based on dry weight of the plant material. Voucher of *P. bartlingianum* (#151560) is kept at the Herbarium of the Museu Paraense Emílio Goeldi. The vouchers of *Piper amapense* and *P. duckei* (#188196 and #188187, respectively) are kept at the Herbarium of the Instituto Nacional de Pesquisas da Amazônia. Plant identification was carried out by the botanist Elsie Franklin Guimarães, Jardim Botânico, Rio de Janeiro, Brazil. The collection data and oil yield are presented in Table 1.

The essential oil was analysed with a GC/MS system (gas chromatograph model VARIAN 3400, mass spectrometer, FINNINGAN model INCOS-XL) with the following conditions: column: DB-5 fused silica (30 m x 0.25mm i.d.; 0.25 μm film thickness); carrier gas: helium, adjusted to a linear velocity of 32 cm/sec (1mL/min) measured at 100ºC; injector temperature: 220°C; temperature programmed: 60°C-240°C (3°C/min); injection type: splitless (1μl of a 1:1000 n-hexane solution); mass spectra: 70 eV (in EI mode). Individual volatile components were identified by comparison of both mass spectra and their GC retention data with those of authentic standards previously stored in the data system. Other identifications were made by comparison of mass spectra with those in the data system libraries and the literature (Adams, 1995). The retention indices were calculated for all volatile constituents using a homologous series of *n*-alkanes. The compounds identified in the oils of *Piper amapense, P. duckei* and *P. bartlingianum* are listed in Table 2.

RESULTS AND DISCUSSION

The essential oils of analysed *Piper* species were characterized by the presence of sesquiterpenes. The major compounds identified in the oil of *P. amapense* were *trans*-caryophyllene (25.0%), β-selinene (15.0%) and caryophyllene oxide (17.0%). The oil of *P. duckei* was dominated by *trans*-caryophyllene (23.5%), caryophyllene oxide (18.4%), β-eudesmol (9.4%) and α-eudesmol (9.1%). The main volatile components found in *P. bartlingianum* were α-cadinol (11.2%), β-elemene (10.5%), α-muurolol (9.4%), (E)-nerolidol. The sesquiterpene hydrocarbons α-copaene, *trans*-caryophyllene and spathulenol were present in the oils of all analysed species. In general, the essential oils of *Piper* species from Amazonia are rich on mono- and ses-

Table 1. Identification, collection data and essential oil yield of the three *Piper* species studied.

Species	Local of collection	Oil (%)
Piper amapense Yunck.	Km 26, Manaus/Itacoatiara highway, AM	0.6
P. duckei C. DC.	Km 26, Manaus/Itacoatiara highway, AM	0.4
P. bartlingianum (Miq.) C.DC.	Km 1, Manaus/Porto Velho highway, AM	0.3

Table 2. Volatile constituents identified in the essential oils of *Piper* species.

Constituents	Retention index	*P. amapense* (%)	P. duckei (%)	*P. bartlingianum* (%)
α-Copaene	1376	2,2	1.6	0.9
β-Elemene	1392			10.5
trans-Caryophyllene	1420	25,0	23.5	5.9
α-Humulene	1451	2,2	3.3	
allo-Aromadendrene	1461	4,1		
γ-Muurolene	1477			3.0
Germacrene D	1481	2,6		
β-Selinene	1488	15,0		
α-Selinene	1496			4.0
trans-β-Guaiene	1502			5.2
1S,*cis*-Calamenene	1524			3.4
Elemol	1550	4,8		
(E)-Nerolidol	1566		2.4	9.0
Spathulenol	1579	5,1	5.2	7.8
Caryophyllene oxide	1584	17,0	18.4	
Globulol	1586			7.7
Guaiol	1599	5,3		
Humulene epoxide II	1610	4.2		
1-*epi*-Cubenol	1629		2.8	8.0
γ-Eudesmol	1631		4.3	
epi-α-Muurolol	1643		3.0	7.3
α-Muurolol	1648		5.7	9.4
α-Cadinol	1658			11.2
β-Eudesmol	1651		9.4	
α-Eudesmol	1653		9.1	
Bulnesol	1669	5.6		

quiterpenes, like the present examples, or arylpropanoids, as cited by Maia *et al.* (1987) and Gottlieb *et al.* (1981).

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