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Leaf essential oils of *Dicypellium caryophyllaceum* (Mart.) Nees (Lauraceae): an almost extinct species in the Amazon

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Abstract

Dicypellium caryophyllaceum, known in Brazil as "pau-cravo" ("clove wood") or "cravo-do-maranhao" ("maranhao clove"), is an almost extinct Lauraceae species due to the intense exploitation of its bark and inflorescences in the past. Essential oils of the leaves of thirteen specimens of *D. caryophyllaceum* were obtained by hydrodistillation and analyzed by GC/MS. Additionally the oil from the twigs of one specimen was studied. All oils showed a high content of eugenol (leaves: 43.70-80.43%; thick twigs: 94.66%; fine twigs: 64.32%), followed by limonene and sylvestrene. Besides eugenol and methyleugenol, 34 compounds were reported here for the first time to *D. caryophyllaceum*. This is the first study on the chemical composition of the leaf and twigs essential oils of this species.

Keywords: *Dicypellium caryophyllaceum*, Lauraceae, Essential oils, Eugenol.

1. Introduction

The family Lauraceae Juss. comprises 52 genera and approximately 3,000 species, distributed throughout tropical to subtropical latitudes[1]. Twenty two genera and about 390 spp. of this family occur in Brazil, mostly in wet forests, sandbanks and "cerrado"[2]. *Dicypellium* Nees & Mart. comprises two species: *D. caryophyllaceum* (Mart.) Nees and *D. manausense* W. A. Rodrigues. *Dicypellium caryophyllaceum* is a tree up to 20 m in height, commonly known in the Brazilian States of Pará and Maranhão as "pau-cravo" ("clove wood") and "cravo-do-maranhao" ("maranhão clove"), in reference to the odor of all organs of the plant[3]. It is a forest species of great interest to conservation programs for species in risk[4]. The intense exploitation since 1660 of the trunk bark and of the inflorescences that were exported to be used as spices in substitution to Indian clove and Ceylon cinnamon[4, 5] almost led to the extinction of *D. caryophyllaceum*. It is a forest species of great interest to conservation programs for species in risk[4]. The medicinal use of the bark and leaves of *D. caryophyllatum* was reported by several authors[5-7]. The trunk wood essential oil of *D. caryophyllaceum* (cited as *D. caryophyllatum*) was reported to contain high amounts of eugenol (95.5%)[8]. Eugenol has several biological properties, including fungicidal[9, 10], anticarcinogenic[11], antiallergic[12, 13], antimutagenic[14], antioxidant[15], insecticidal[16] and anti-inflammatory and peripheral antinociceptive activities[17]. The aim of the present study was to investigate the chemical composition of the leaf and twigs essential oils of *D. caryophyllaceum* growing wild in the State of Pará.

2. Material and methods

2.1 Material

Samples of leaves and twigs were collected (2008 to 2012) in the Municipality of Altamira, State of Para, Brazil. The botanical identification was made by N. A. Rosa, from Museu Paraense Emílio Goeldi (MPEG) and the voucher was kept in the Herbarium MG (# 185,536) of MPEG.

2.2 Extraction of volatile compounds

The samples were dried for 7 days in an air-conditioned room (at low humidity) and then ground.

Leaves (50 g) were hydrodistilled for 3h, using a Clevenger-type apparatus with maintenance of the refrigeration water at 15 ºC. The oils obtained were centrifuged for 5 min (3,000 rpm), dried over Na_2SO_4 and centrifuged again in the same conditions. The hexane solution (1 mL) containing 2 µL of the oil was submitted to GC/FID and GC/MS analysis. The total oil yield was expressed in percentage (volume/mass) on the basis of dried material. The amount of water was measured using infrared light on a Mater 50 device.

2.3 Analysis of the volatiles

The oils were analyzed using a Shimadzu GC/MS Model QP 2010 Plus, equipped with a Rtx-5MS (30 m x 0.25 mm; 0.25 µm film thickness) fused silica capillary column. Chromatographic conditions: helium as carrier gas at 1.2 mL.min^{-1}; splitless injection of 1 µL of the hexane solution; injector and interface temperature at 250 °C; oven temperature program 60-240 °C at 3 °C.min^{-1}; EIMS electron energy, 70 eV with ion source temperature at 200 ºC. Identification of the compounds were made by comparison of their GC mass and retention data with those in NIST-05 library and cited in the literature data [18]. Retention indices were calculated using *n*-alkane standard solutions (C8-C26) available from Fluka S. A., in the same chromatographic conditions.

Table 1: Volatiles (%) identified in the leaf oils of *Dicypellium caryophyllaceum*

Constituents	RI*	A	B	C	D	E	F	G	H	I	J	L	M	N
α-thujene	928	0.14	0.07		0.09									
α-pinene	936	3.78	3.37	2.61	3.92	3.09	2.39	2.14	3.07	2.67	2.38	2.41	3.02	0.57
β-pinene	981	1.93	1.45	1.29	1.78	1.46	1.12	0.95	1.55	1.34	1.15	1.16	1.44	
myrcene	993	2.68	1.44	1.48	2.01	0.67	0.95	0.56	0.79	1.26	1.21	1.27	0.93	0.19
α-phellandrene	1008	4.37	2.41	3.16	4.82	0.91	1.71	0.75	0.93	3.60	3.13	2.40	4.10	0.45
p-cymene	1027		2.26	1.87	3.75	2.57	2.04	2.04	2.01	1.96	1.72	2.24	3.14	0.29
limonene + sylvestrene	1031	39.82	28.08	26.55	31.57	24.01	22.86	19.05	24.94	25.83	22.17	24.87	22.64	7.13
(*E*)-β-ocimene	1049				tr									
γ-terpinene	1060				tr									
terpinolene	1091	0.14			0.17									
linalool	1102	0.45	0.27	0.24	0.41	0.20	0.14	0.12	0.11	0.19	0.14	0.27	0.24	
terpinen-4-ol	1180	0.13	0.11		0.16	0.07	0.06	0.07			0.07	0.11		
p-cymen-8-ol	1187				0.05									
α-terpineol	1193	0.24	0.10	0.18	0.36		0.20	0.11	0.30	0.10	0.12	0.15	0.09	
trans-carveol	1221				0.09									
cis-p-mentha-1(7),8-dien-2-ol	1230				0.06									
carvone	1247				tr									
geraniol	1256	0.26	0.25	0.21	0.33	0.26	0.29	0.16	0.23	0.17	0.14	0.20	0.27	
safrole	1292	0.38			tr									
carvacrol	1304				tr									
α-cubebene	1353	0.02	0.05	0.05	0.10		0.14	0.05				0.05	0.10	0.11
eugenol	1361	44.83	55.54	55.95	43.70	64.17	65.85	71.91	64.78	58.43	58.81	54.23	58.81	80.43
geranyl acetate	1386	0.02	0.06	0.11	0.18					0.09	0.19		0.17	
methyleugenol	1408	0.25	0.40	0.18	0.32	0.36	0.59	0.42	0.42	0.37	0.38	0.29	0.28	0.17
β-caryophyllene	1425	0.29	0.84	0.78	1.14	0.44	0.98	0.46	0.44	0.96	0.84	0.69	1.55	1.29
isoeugenol	1454	0.03	0.04		tr	0.05	0.05	0.05	0.05	0.04	0.04	0.04		0.07
α-humulene	1458	0.03	0.06	0.06	0.10	0.04	0.08	0.05	0.04	0.07	0.07	0.05	0.12	0.10
β-selinene	1492					0.55								
α-selinene	1500					0.15								
(*E*,*E*)-α-farnesene	1511	0.02		0.07	0.12	0.17		0.09						
δ-cadinene	1527				0.04		0.08	0.09	0.03				0.06	0.10
eugenyl acetate	1530	0.02	2.60	4.97	3.92	0.08		0.25		2.60	7.06	1.95	2.26	0.09
(*E*)-nerolidol	1563							0.03						
caryophyllene oxide	1585	0.11	0.43	0.17	0.38	0.37	0.31	0.43	0.27	0.21	0.27	0.27	0.51	0.43
tetracosane	2400													2.35
Monoterpene hydrocarbons		52.86	39.08	36.96	48.11	32.71	31.07	25.49	33.29	36.66	31.76	34.35	35.27	8.63
Oxygenated monoterpenes		0.82	0.48	0.42	1.13	0.27	0.40	0.30	0.41	0.29	0.33	0.53	0.33	-
Sesquiterpene hydrocarbons		0.36	0.95	0.96	1.50	1.35	1.28	0.74	0.51	1.03	0.91	0.79	1.83	1.60
Oxygenated sesquiterpenes		0.11	0.43	0.17	0.38	0.37	0.31	0.46	0.27	0.21	0.27	0.27	0.51	0.43
Phenylpropanoids		45.79	58.89	61.42	48.45	64.92	66.78	72.79	65.48	61.70	66.62	56.71	61.79	80.76
Alkane		-	-	-	-	-	-	-	-	-	-	-	-	2.35
Total		99.94	99.83	99.93	99.65	99.62	99.84	99.78	99.96	99.89	99.89	92.65	99.73	95.99

*RI on Rtx-5MS; tr = traces (< 0.02%);

3. Results and Discussions

The percentage of the compounds identified in the leaf oils are listed in Table 1 in sequence of their retention indices. Higher yield in oils were obtained from the leaves (0.90-7.21%), while the fine twigs and thick twigs furnished 2.93% and 1.08%, respectively. A total of 36 compounds were identified. The chemical composition of the essential oils of *D. caryophyllaceum* was characterized by the presence of monoterpenes, sesquiterpenes and phenylpropanoids with the leaf essential oil consisting of monoterpene hydrocarbons (8.63-52.86%), oxygenated monoterpenes (zero-1.13%), sesquiterpene hydrocarbons (0.36-1.89%), oxygenated sesquiterpenes (0.11-0.51%),

phenylpropanoids (45.79-80.76%), and *n*-alkanes (1.40-2.35%).

All oils of *D. caryophyllaceum* showed a high content of eugenol (leaves: 43.70-80.43%; thick twigs: 94.66%; fine twigs: 64.32%). Besides eugenol, limonene + sylvestrene (4.78%), methyleugenol (0.20%), *trans*-calamenene (0.07%) and eugenyl acetate (0.12%) were detected in the oil from the thick twigs, while α-pinene (2.32%), camphene (0.14%), β-pinene (1.11%), myrcene (1.21%), α-phellandrene (2.70%), *p*-cymene (traces), limonene + sylvestrene (27.13%), α-cubebene (0.06%), methyleugenol (0.14%), β-caryophyllene (0.41%) and eugenyl acetate (0.35%) were detected in the oil of fine twigs. A mixture of the monoterpenes limonene and sylvestrene was also detected in high contents in all analyzed oils. Except for eugenol and methyeugenol, all other 34 detected compounds were reported for the first time to *D. caryophyllaceum*. Our results showed that leaves and twigs of *D. caryophyllaceum* furnished oils rich in eugenol, in the same way of the trunk wood, previously studied by Alencar and coworkes[8].

It has been observed that the odors of *D. caryophyllaceum* and *Cinnamomum verum* J. Pressl ("Indian cinnamon") are very similar, as well as the taste of *D. caryophyllaceum* and the buds of clove (*Eugenia caryophylata*)[5]. Chemical studies of the essential oils of *C. verum* showed diversity on the composition. Eugenol (60%) and linalool (85.7%) were the major compounds in the leaf oils of specimens collected in Brazil and South India, respectively [19, 20]; (E)- cinnamaldehyde[21] and methyl benzoate are often found [22].

The high content of eugenol, as well the high yield oil in leaves of *D. caryophyllaceum* could be other important source of rich-eugenol oil, but urgent conservations programs focused in *D. caryophyllaceum* must be improved before extinction of this important species.

4. Conclusion

This study shows that the leaves of *D. caryophyllaceum* are a potential source of a rich-containing eugenol essential oil.

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6. References

1. Chanderbali AS, Werff H, Renner VDSS. Phylogeny and historical biogeography of Lauraceae: evidence from the chloroplast and nuclear genomes. Annals of the Missouri Botanical Garden 2001; 88:104-134.
2. Barroso GM, Guimarães EF, Ichaso CLF, Costa CG, Peixoto AL. Sistemática de angiospermas do Brasil. Edn 2ª, Vol. 1, Universidade Federal de Viçosa, Viçosa, 2002.
3. Rizzini CT, Mors WB. Botânica econômica brasileira. EPU/EDUSP. São Paulo, 1976.
4. Salomão RP, Rosa NA. Pau-cravo: 'droga do sertão' em risco de extinção. Ciência Hoje 2012; 49:46-50.
5. Corrêa MP. Dicionário das plantas úteis do Brasil e das exóticas cultivadas. IBDF. Rio de Janeiro, 1984.
6. Le Cointe P. Árvores e plantas úteis (indígenas e aclimadas): nomes vernáculos e nomes vulgares, classificação botânica, habitat, principais aplicações e propriedades. Edn 2, Companhia Editora Nacional, São Paulo, 1947.
7. Vieira LS. Fitoterapia da Amazônia: manual de plantas medicinais (a farmácia de Deus). Edn 2, Agronômica Ceres, São Paulo, 1992.
8. Alencar R, Lima RA, Corrêa RGC, Gottlieb OR, Marx MC, Silva ML, Maia JGS, Magalhães MT, Assumpção RMV. Óleos essenciais de plantas brasileiras. Acta Amazononica 1971; 1(3):41-43.
9. Gayoso CW, Lima EO, Olivera VT, Pereira FO, Souza EL, Lima EL, Navarro DF. Sensitivity of fungi isolated from onichomicosis to *Eugenia caryophyllata* essential oil and eugenol. Fitoterapia 2005; 76:247-249.
10. Manohar V, Ingram C, Gray J, Talpur NA, Echard BW, Bagchi D, Preuss HG. Antifungal activities of origanum oil against *Candida albicans.* Mololecular and Cellular Biochemistry 2001; 228:111-117.
11. Zeng GQ, Kenney PM, Lam LKT. Sesquiterpenes from clove (*Eugenia caryophyllata*). Journal of Natural Products 1992; 55:99-1003.
12. Kim HM, Lee EH, Hong SH, Song HJ, Shin MK, Kim SH, Shin TY. Effect of *Syzygium aromaticum* extract on immediate hypersensitivity in rats. Journal of Ethnopharmacology 1998; 60:125-131.
13. Corrêa MFP, Melo GO, Costa SS. Substâncias de origem vegetal potencialmente úteis na terapia da asma. Revista Brasileira de Farmacognosia 2008; 18 (Supl):785-797.
14. Miyazawa M, Hisama M. Suppression of chemical mutagen induced SOS response by alkylphenols from clove (*Syzygium aromaticum*) in *Salmonella typhymurium* TA1535/pSK1002 umu test. Journal of Agricultural Food Chemistry 2001; 49:4019-4025.
15. Ogata M, Hoshi M, Urano S, Endo T. Antioxidant activity of eugenol and related monomeric and dimeric compounds. Chemical Pharmaceutical Bulletin 2000; 48:1467-1469.
16. Park IK, Lee HS, Lee SG, Park JD, Ahn YJ. Insecticidal and fumigant activities of *Cinnamomum cassia* bark-derived material against *Mechoris ursulus* (Coleoptera Attelabidae). Journal of Agricultural Food Chemistry 2000; 48:2528-2531.
17. Daniel AN, Sartoretto SM, Schmidt G, Caparroz-Assef SM, Bersani-Amado CA, Cuman RKN. Anti-inflammatory and antinociceptive activities of eugenol essential oil in experimental animal models. Revista Brasileira de Farmacognosia 2009; 19(1B):212-217.
18. Adams RP. Identification of essential oil components by gas chromatography/mass spectrometry. Edn 4, Allured Pub Corp, Carol Stream IL, 2007, 804.
19. Lima MP, Zoghbi MGB, Andrade EHA, Silva TMD, Fernandes CS. Constituintes voláteis das folhas e dos galhos de *Cinnamomum zeylanicum* Blume (Lauraceae). Acta Amazonica 2005; 35(3):363-366.
20. Jirovetz L, Buchbauer G, Ruzicka J, Shafi MP, Rosamma MK. Analysis of *Cinnamomum zeylanicum* blume leaf oil from South India. J Essent Oil Res 2001; 13:442-443.
21. Möllenbeck S, König T, Schreier P, Schwab W, Rajaonarivony J, Ranarivelo L. Chemical composition and analyses of enantiomers of essential oils from Madagascar. Flav Fragr J 1997; 12:63-69.
22. Rao YR, Paul SC, Dutta PK. Major constituents of essential oils of *Cinnamomum zeylanicum*. Indian Perfumer 1988; 32(1):86-89.