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Artigo

# VOLATILE CONSTITUENTS OF THE OILS FROM *Povedadaphne quadriporata* (LAURACEAE) FROM "ALBERTO M. BRENES" BIOLOGICAL PRESERVE, COSTA RICA

**José F. Cicció* and Carlos Chaverri**
Centro de Investigaciones en Productos Naturales and Escuela de Química, Universidad de Costa Rica, 2060 San José, Costa Rica

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The composition of the leaf, bark and wood oils of *Povedadaphne quadriporata* W. Burger from Costa Rica were analyzed by capillary GC/FID and GC/MS. One hundred and sixty-three compounds were identified. The major components from the leaf oil were α-pinene (21.2%), germacrene D (18.1%), β-pinene (14.8%), α-phellandrene (7.8%), α-copaene (6.6%), β-caryophyllene (6.1%) and δ-cadinene (3.5%). From bark oil, the main constituents were α-pinene (27.7%), *p*-cymene (7.8%), β-pinene (7.4%), camphene (3.6%), α-copaene (3.5%) and limonene (3.3%). From wood oil, 1,10-di-*epi*-cubenol (8.0%), α-eudesmol (3.4%), cadalene (3.4%) and δ-cadinene (3.0%) were the major compounds identified. This paper describes for the first time the composition of essential oils in this unique species and genus.

Keywords: *Povedadaphne quadriporata*; Lauraceae; essential oils.

## INTRODUCTION

The Lauraceae is a family constituted of about 50 genera and includes 2000 to 3000 species of mostly trees from the tropics.[1-4] This family is well distributed and ecologically important in the Costa Rican cloud forests. Many individuals appear in abundance and diversity.[5] Taxonomically, this family is recognized by the simple, alternate, stiff and aromatic elliptic to obovate leaves, and by the fruits often borne in a cup. In Costa Rica, there are found about 130 species representing 18 genera, were the most diverse is *Ocotea* Aubl.[6] About 37% of the species and two genera (*Gamanthera* and *Povedadaphne*) are endemic to Costa Rican forest. Worldwide, the family has a considerable economic value because it is used as a source of timber for construction and furniture. Also, some species are utilized for food (*Persea americana* Mill., Avocado), spices (*Laurus nobilis* L., Bay Laurel and *Cinnamomum verum* J. Presl, Cinnamon), aromatics [*Sassafras albidum* (Nutt.) Ness, Sassafras, *Aniba rosaeodora* Ducke, Rosewood] and medicines [*Cinnamomum camphora* (L.) J. Presl, Camphor Laurel].

*Povedadaphne* is a single species genus only known in Costa Rica. The plant *Povedadaphne quadriporata* W. Burger[3,7] is a tree about 20 m tall. It can be found distributed in Costa Rica between 200 and 1000 m about sea level in the very wet premontane rain forest of the North Caribbean. The plant presents small stiff, slightly lustrous olive green (when dry), obovate-elliptic leaves, with conspicuous small pit domatia with white hairs in the vein axils of the lower surface. The leaf base is narrow and decurrent. The flowers are small with nine hairy stamens dehiscing by four apical pores. The fruit is globose or pyriform. The wood is pinkish and used in construction. When the leaves are crushed they give off a scent due to an oil of unknown composition which has not been previously reported. The aim of this work was to examine the chemical composition of the oils obtained from fresh leaves, bark and wood of *P. quadriporata*. This tree is rare and endemic to Costa Rica. Popularly known as "ira rosa" it is classified as "Vulnerable" according IUCN Status[8] with a high risk of extinction in the wild in the medium-term future because the population is restricted to small locations.

*e-mail: jfciccio@gmail.com

## EXPERIMENTAL

### Plant material

Leaves, bark and wood of *Povedadaphne quadriporata* W. Burger were collected in May, in the tropical premontane rain forest of the "Alberto M. Brenes" Biological Preserve, located in the valley of the Río San Lorencito, San Ramón, Province of Alajuela, in north-central Costa Rica, at an elevation of 800 m. A voucher specimen was deposited at the Herbarium of the University of Costa Rica (USJ 44865).

### Oil isolation

Fresh leaves (1 kg) were subjected to hydrodistillation for 2 h using a modified Clevenger-type apparatus. The distilled oil was collected and dried over anhydrous sodium sulfate, filtered and stored in a freezer (0-10 °C). The colorless oil yield was 0.2% (v/w). The yields from bark and wood were 0.1% (v/w).

### General analytical procedures

*GC/FID analysis*

The oils of *P. quadriporata* were analyzed by GC/FID using a Shimadzu GC-17 gas chromatograph. The data were obtained on a 5% phenyl- 95% methylpolysiloxane fused silica capillary column (30 m x 0.25 mm; film thickness 0.20 μm), Heliflex (Alltech) AT-5, with a Shimadzu Class-VP, version 4.3 software. Operating conditions were: carrier gas $N_2$, flow 1.0 mL/min; oven temperature program: 60-220 °C at 3 °C/min, 220 °C (10 min); sample injection port temperature 250 °C; detector temperature 275 °C; split 1:50.

*GC/MS analysis*

The analysis by GC/MS was performed using a Shimadzu GC-17A gas chromatograph coupled with GCMS-QP5050 apparatus and CLASS 5000 software with Wiley139 computer database. The data were obtained on a 5% phenyl- 95% methylpolysiloxane fused silica capillary column (30 m x 0.25 mm; film thickness 0.25 μm).

Operating conditions were: carrier gas He, flow 1.0 mL/min; oven temperature program: 60-240 °C at 3 °C/min; sample injection port temperature 250 °C; detector temperature 260 °C; ionization voltage: 70 eV; ionization current 60 µA; scanning speed 0.5 s over 38-400 amu range; split 1:70.

### Identification

Identification of the components of the oils was performed using the retention indices on a DB-5 type column, and by comparison of their mass spectra with those published in the literature[9-11] or those of our own database. Integration of the total chromatogram, expressed as area percent, has been used to obtain quantitative compositional data.

## RESULTS AND DISCUSSION

The oils obtained from leaves, bark and wood of *P. quadriporata* were predominantly terpenoid in nature. The chemical analysis of the leaf oil showed that the major classes of constituents were monoterpene and sesquiterpene hydrocarbons (48.9% and 45.2% respectively). Among the 86 compounds identified (Table 1), comprising about 99% of the total oil, the major constituents of the oil were α-pinene (21.2%), germacrene D (18.1%), β-pinene (14.8%), α-phellandrene (7.8%), α-copaene (6.6%), β-caryophyllene (6.1%) and δ-cadinene (3.5%). The oxygenated compounds amount only to about 5%.

From bark oil, the monoterpene and sesquiterpene hydrocarbons were 52.4% and 17.0% respectively. The oxygenated compounds were more abundant (24.6%) than encountered in the leaf oil. The 116 compounds identified represent about 97% of the oil. The major components of the oil were α-pinene (27.7%), *p*-cymene (7.8%), β-pinene (7.4%), camphene (3.6%), α-copaene (3.5%) and limonene (3.3%), as well as a significant number of cadinane, guaiane and eudesmane-type sesquiterpenoids.

The wood oil is composed mainly of sesquiterpenoids. Of the 87 compounds identified, 1,10-di-*epi*-cubenol (8.0%) was the major constituent together with α-eudesmol (3.4%), cadalene (3.0%), δ-cadinene (3.0%) and γ-eudesmol (2.7%). Some constituents from this oil needed further identification.

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**Table 1.** Composition of the oils isolated from leaf, bark and wood of *Povedadaphne quadriporata* Burger

| Compound[a] | RI[b] | Leaves (%) | Bark (%) | Wood (%) | Identification method[d] |
|---|---|---|---|---|---|
| hexanal | 808 | | t | | 1, 2 |
| 2-(*E*)-hexenal | 854 | t | | | 1, 2 |
| 2-heptanone | 894 | | t | | 1, 2 |
| tricyclene | 926 | t | 0.1 | t | 1, 2 |
| α-thujene | 931 | 0.1 | t | | 1, 2 |
| α-pinene | 937 | 21.2 | 27.7 | 1.2 | 1, 2, 3 |
| α-fenchene | 948 | t | t | t | 1, 2 |
| camphene | 952 | 0.7 | 3.6 | 0.8 | 1, 2 |
| benzaldehyde | 963 | | | 0.1 | 1, 2 |
| verbenene | 967 | | 0.1 | | 1, 2 |
| sabinene | 976 | t | | | 1, 2 |
| β-pinene | 979 | 14.8 | 7.4 | 0.2 | 1, 2, 3 |
| 6-methyl-5-hepten-2-one | 990 | | 0.1 | | 1, 2 |
| myrcene | 992 | 1.1 | 0.2 | 0.2 | 1, 2, 3 |
| α-phellandrene | 1007 | 7.8 | 1.2 | 0.2 | 1, 2, 3 |
| δ-3-carene | 1012 | 0.2 | 0.1 | | 1, 2 |
| α-terpinene | 1019 | 0.1 | 0.1 | 0.2 | 1, 2, 3 |
| *p*-cymene | 1025 | 1.1 | 7.8 | 0.2 | 1, 2 |
| limonene | 1031 | 1.1 | 3.3 | 0.2 | 1, 2, 3 |
| 1,8-cineole | 1033 | 0.3 | 0.4 | 0.2 | 1, 2, 3 |
| (*Z*)-β-ocimene | 1039 | 0.1 | | | 1, 2 |
| (*E*)-β-ocimene | 1049 | 0.1 | | | 1, 2 |
| γ-terpinene | 1059 | 0.2 | 0.2 | | 1, 2 |
| *cis*-sabinene hydrate | 1069 | t | | | 1, 2 |
| *trans*-linalool oxide | 1076 | | | 0.2 | 1, 2 |
| *p*-mentha-2,4(8)-diene | 1086 | t | t | | 1, 2 |
| terpinolene | 1088 | 0.4 | 0.6 | | 1, 2 |
| fenchone | 1090 | | | 0.2 | 1, 2 |
| linalool | 1098 | t | 0.1 | 0.4 | 1, 2, 3 |
| α-pinene oxide | 1099 | | t | | 1, 2 |
| endo-fenchol | 1114 | t | 1.6 | 0.2 | 1, 2 |
| *trans*-pinene hydrate | 1122 | t | | 0.1 | 1, 2 |
| exo-fenchol | 1124 | | 0.1 | | 1, 2 |
| α-campholenal | 1126 | | 1.0 | 0.2 | 1, 2 |

**Table 1.** continuation

| Compound[a] | RI[b] | Leaves (%) | Bark (%) | Wood (%) | Identification method[d] |
|---|---|---|---|---|---|
| nopinone | 1138 | t | 0.9 | 0.1 | 1, 2 |
| *trans*-pinocarveol | 1142 | t | t | | 1, 2 |
| camphor | 1145 | | t | 0.1 | 1, 2 |
| *trans*-verbenol | 1147 | t | | | 1, 2 |
| camphene hydrate | 1148 | t | 0.4 | 0.2 | 1, 2 |
| isoborneol | 1158 | | t | | 1, 2 |
| *trans*-pinocamphone | 1163 | | t | | 1, 2 |
| pinocarvone | 1164 | t | t | | 1, 2 |
| borneol | 1165 | 0.1 | 1.5 | 0.4 | 1, 2 |
| *cis*-pinocamphone | 1173 | | t | | 1, 2 |
| terpinen-4-ol | 1177 | 0.2 | 0.3 | 0.1 | 1, 2, 3 |
| *p*-cymen-8-ol | 1179 | | | t | 1, 2 |
| α-terpineol | 1191 | 0.1 | 2.0 | 0.3 | 1, 2, 3 |
| mirtenol | 1196 | t | 0.2 | 0.1 | 1, 2 |
| myrtenal | 1197 | t | | | 1, 2 |
| *cis*-piperitol | 1198 | t | | | 1, 2 |
| *trans*-dihydrocarvone | 1203 | | 0.1 | | 1, 2 |
| verbenone | 1206 | | t | | 1, 2 |
| *trans*-carveol | 1220 | | 0.4 | | 1, 2 |
| sabinene hydrate | 1220 | | | t | 1, 2 |
| cumin aldehyde | 1239 | | 0.2 | 0.6 | 1, 2 |
| carvone | 1244 | | t | 0.1 | 1, 2 |
| carvotanacetone | 1248 | t | 0.4 | 0.1 | 1, 2 |
| piperitone | 1251 | | | t | 1, 2 |
| carvenone | 1256 | | t | | 1, 2 |
| *trans*-myrtanol | 1259 | | | t | 1, 2 |
| perilla aldehyde | 1272 | | | 0.1 | 1, 2 |
| *p*-ment-1-en-7-al | 1277 | | t | | 1, 2 |
| bornyl acetate | 1285 | | t | | 1, 2 |
| *p*-cymen-7-ol | 1287 | | t | | 1, 2 |
| thymol | 1289 | | | t | 1, 2 |
| carvacrol | 1298 | | t | t | 1, 2 |
| undecanal | 1306 | | t | t | 1, 2 |
| δ-elemene | 1338 | t | t | | 1, 2 |
| α-cubebene | 1350 | 0.3 | t | 0.2 | 1, 2 |
| cyclosativene | 1369 | | 0.1 | 0.1 | 1, 2 |
| α-ylangene | 1371 | 0.1 | 0.2 | 0.6 | 1, 2 |
| α-copaene | 1374 | 6.6 | 3.5 | 0.1 | 1, 2 |
| β-bourbonene | 1384 | t | t | | 1, 2 |
| β-cubebene | 1390 | 0.9 | t | | 1, 2 |
| β-elemene | 1393 | t | | 0.1 | 1, 2 |
| sativene | 1396 | | t | | 1, 2 |
| cyperene | 1398 | t | t | | 1, 2 |
| dodecanal | 1408 | | 0.3 | 0.3 | 1, 2 |
| α-gurjunene | 1411 | t | t | 0.1 | 1, 2 |
| α-*cis*-bergamotene | 1416 | | t | | 1, 2 |
| β-caryophyllene | 1418 | 6.1 | 0.4 | 1.3 | 1, 2, 3 |
| α-santalene | 1421 | | 0.4 | 0.4 | 1, 2 |
| β-ylangene | 1422 | 0.1 | | | 1, 2 |
| β-copaene | 1428 | 0.6 | t | | 1, 2 |
| β-gurjunene | 1429 | | t | | 1, 2 |
| γ-elemene | 1433 | t | | | 1, 2 |
| α-*trans*-bergamotene | 1436 | | 0.5 | t | 1, 2 |
| α-guaiene | 1440 | 0.3 | t | | 1, 2 |
| aromadendrene | 1440 | | | 0.1 | 1, 2 |
| *trans*-muurola-3,5-diene | 1445 | t | t | | 1, 2 |
| α-humulene | 1453 | 1.9 | 0.1 | 0.1 | 1, 2, 3 |
| geranylacetone | 1457 | | t | | 1, 2 |
| alloaromadendrene | 1459 | 1.1 | 2.2 | 0.9 | 1, 2 |
| *cis*-muurola-4(14),5-diene | 1462 | t | | | 1, 2 |

**Table 1.** continuation

| Compound[a] | RI[b] | Leaves (%) | Bark (%) | Wood (%) | Identification method[d] |
|---|---|---|---|---|---|
| 9-*epi*-caryophyllene | 1466 | | t | | 1, 2 |
| γ-gurjunene | 1471 | | | 0.2 | 1, 2 |
| drima-7,9(11)-diene | 1473 | | t | | 1, 2 |
| γ-muurolene | 1477 | | | 0.1 | 1, 2 |
| germacrene D | 1481 | 18.1 | | 0.7 | 1, 2 |
| α-amorphene | 1482 | | 0.2 | 0.9 | 1, 2 |
| β-selinene | 1485 | 1.0 | 1.8 | 1.4 | 1, 2 |
| valencene | 1490 | | 1.2 | | 1, 2 |
| viridiflorene | 1492 | t | | | 1, 2 |
| *epi*-cubebol | 1492 | t | | 0.9 | 1, 2 |
| *trans*-muurola- 4(14),5-diene | 1492 | 0.1 | | | 1, 2 |
| bicyclogermacrene | 1495 | 1.7 | | | 1, 2 |
| α-himachalene | 1497 | | | 0.1 | 1, 2 |
| α-muurolene | 1499 | 0.5 | 1.6 | 0.5 | 1, 2 |
| *cis*-β-bisabolene | 1505 | | 1.6 | | 1, 2 |
| α-bulnesene | 1506 | 0.1 | | | 1, 2 |
| γ-cadinene | 1514 | 1.4 | 0.9 | 0.2 | 1, 2 |
| cubebol | 1518 | | | 0.7 | 1, 2 |
| δ-cadinene | 1524 | 3.5 | 2.3 | 3.0 | 1, 2, 3 |
| *trans*-cadina-1(2),4-diene | 1530 | 0.5 | t | 0.2 | 1, 2 |
| α-cadinene | 1536 | 0.3 | 0.1 | | 1, 2 |
| α-calacorene | 1541 | t | t | 1.5 | 1, 2 |
| *cis*-muurolol-5-en-4-β-ol | 1543 | | 0.7 | | 1, 2 |
| elemol | 1550 | 0.3 | 1.7 | 0.2 | 1, 2 |
| elemicine | 1555 | | t | | 1, 2 |
| β-calacorene | 1563 | | t | 0.5 | 1, 2 |
| germacrene B | 1564 | 0.1 | | | 1, 2 |
| norolidol | 1565 | | | 1.8 | 1, 2 |
| 1,5-epoxysalvial-4(14)-ene | 1572 | t | t | 1.3 | 1, 2 |
| (*Z*)-isoelemicine | 1573 | | 0.1 | | 1, 2 |
| spathulenol | 1576 | 0.2 | t | 1.1 | 1, 2 |
| caryophyllene oxide | 1582 | 0.3 | 0.3 | | 1, 2 |
| globulol | 1584 | | 0.1 | 1.2 | 1, 2 |
| gleenol | 1585 | | 0.1 | | 1, 2 |
| viridiflorol | 1590 | 0.3 | 0.1 | 1.0 | 1, 2 |
| salvial-4(14)-en-1-one | 1593 | t | t | | 1, 2 |
| guaiol | 1596 | 0.4 | 1.6 | 0.9 | 1, 2 |
| humulene epoxyde II | 1606 | 0.1 | 0.1 | 1.3 | 1, 2 |
| 1,10-di-*epi*-cubenol | 1613 | t | | 8.0 | 1, 2 |
| tetradecanal | 1614 | | 1.6 | | 1, 2 |
| 1-*epi*-cubenol | 1627 | 0.3 | 1.3 | | 1, 2 |
| γ-eudesmol | 1632 | | 1.5 | 2.7 | 1, 2 |
| β-acorenol | 1635 | 0.1 | | 0.4 | 1, 2 |
| epi-α-cadinol (τ-cadinol) | 1641 | 0.2 | 1.8 | 1.7 | 1, 2 |
| cubenol | 1642 | | | 1.8 | 1, 2 |
| epi-α-muurolol (τ-muurolol) | 1645 | 0.3 | t | | 1, 2 |
| α-muurolol | 1647 | 0.3 | | | 1, 2 |
| β-eudesmol | 1649 | | t | t | 1, 2 |
| α-eudesmol | 1653 | | 2.6 | 3.4 | 1, 2 |
| α-cadinol | 1655 | 1.4 | 2.9 | | 1, 2 |
| *cis*-calamenen-10-ol | 1661 | t | | | 1, 2 |
| bulnesol | 1668 | | 0.1 | 2.9 | 1, 2 |
| cadalene | 1672 | | | 3.4 | 1, 2 |
| (+)-(4S,8R)-8-*epi*-β-bisabolol | 1672 | | 0.1 | | 1, 2 |
| β-costol | 1684 | | t | 0.8 | 1, 2 |
| eudesma-4(15),7-dien-1-β-ol | 1687 | t | | 1.0 | 1, 2 |
| γ-costol | 1687 | | t | | 1, 2 |
| α-costol | 1692 | | t | | 1, 2 |
| heptadecane | 1700 | | t | | 1, 2 |
| tetradecanoic acid | 1765 | | | 0.6 | 1, 2 |

**Table 1.** continuation

| Compound[a] | RI[b] | Leaves (%) | Bark (%) | Wood (%) | Identification method[d] |
|---|---|---|---|---|---|
| pentadecanal | 1718 | | t | 1.2 | 1, 2 |
| mint sulfide | 1743 | t | | | 1, 2 |
| α-cyperone | 1782 | | | 2.2 | 1, 2 |
| *iso*-costic acid methyl ester | 1798 | | | 1.5 | 1, 2 |
| octadecane | 1800 | | t | | 1, 2 |
| hexadecanal | 1820 | | 0.1 | 0.2 | 1, 2 |
| hexadecanoic acid | 1981 | | | 0.1 | 1, 2 |
| eicosane | 2000 | | 0.1 | | 1, 2 |
| heneicosane | 2100 | | 0.2 | | 1, 2 |
| Monoterpene hydrocarbons | | 48.9 | 52.4 | 2.8 | |
| Oxygenated monoterpenes | | 0.7 | 9.6 | 3.0 | |
| Sesquiterpene hydrocarbons | | 45.2 | 17.0 | 16.7 | |
| Oxygenated sesquiterpenes | | 4.4 | 15.0 | 36.8 | |
| Others | | t | 2.3 | 3.4 | |

[a]Compounds listed in order of elution from 5% phenyl- 95% methylpolysiloxane column. [b]RI = Retention index relative to n-alkanes on the 5% phenyl- 95% methylpolysiloxane column. [c]t = Traces (<0.05%). [d]Method: 1 = Retention Index in 5% phenyl- 95% methylpolysiloxane column; 2 = MS spectra ; 3 = Standard.

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