SHORT REPORT

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records of natural products

Volatile Constituents of Three *Myrsine* L. Species from Brazil

Arthur L. Corrêa[1], Hildegardo S. França[2], Luis Armando C. Tietbohl[1], Bruna N. Luna[3], Marcelo G. Santos[4], Maria de Fátima Freitas[3], Adriana P. Oliveira[*5] and Leandro Rocha[1]

[1]*Department of Pharmaceutical Technology, Faculty of Pharmacy, Fluminense Federal University, Rua Mário Viana 523, 24241000, Niterói, RJ, Brazil*
[2]*Federal Institute of Education Science and Technology of Espírito Santo, Av Ministro Salgado Filho, s/n, 29106010, Vila Velha, ES, Brasil*
[3]*Research Institute for Botanical Garden of Rio de Janeiro, Scientific Resource Board, Rua Pacheco Leão 915, 22460-030, Rio de Janeiro, Brazil*
[4]*Department of Sciences, Faculty of Professors Degree, Rio de Janeiro State University, R. Dr. Francisco Portela 1470, 24435-005, São Gonçalo, RJ, Brazil*
[5]*Department of Drugs and Medicines, Faculty of Pharmacy, Federal University of Rio de Janeiro, Av.Carlos Chagas Filho 373, 21941902, Rio de Janeiro, RJ, Brazil*

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Abstract: The chemical compositions of the essential oils obtained by hydrodistillation from the aerial parts of *Myrsine rubra*, *Myrsine gardneriana* and *Myrsine parvifolia* and the fruits of *Myrsine parvifolia* were elucidated by a combination of GC and GC-MS analyses. The main constituents of the native *M. parvifolia* were caryophyllene oxide (14.4%), β-caryophyllene (12.6%) and γ-Muurolene (7.9%) of the leaves oil and β-caryophyllene (11.7%), δ-Cadinene (7.1%) of the fruit oil. The volatile oil of the endemic *M. rubra* leaves was dominated by β-caryophyllene (17.2%), γ-Muurolene (11.1%), Germacrene B (10.0%). The essential oil of the native *M. gardneriana* leaves was characterized by β-caryophyllene (18.0%), γ-Muurolene (8.4%). These three *Myrsine* species are similar in the dominance of sesquiterpenes. By contrast, monoterpenes were found only in the volatile oil from the fruits of *M. parvifolia*. To the best of our knowledge, this study is the first report on the volatile constituents of *M. rubra*, *M. gardneriana, M. parvifolia*.

Keywords: *Myrsine rubra*; *Myrsine gardneriana*; *Myrsine parvifolia*; essential oil.

1. Plant Source

The fruits and the leaves of *Myrsine parvifolia* A.DC. and the leaves of *Myrsine rubra* M.F.Freitas & Kin.-Gouv. were collected in May 2013 and June 2010, in Restinga de Jurubatiba National Park, Rio de Janeiro State (Brazil), respectively. The plants were identified by Dr. Marcelo Guerra Santos, Universidade do Estado do Rio de Janeiro, Brazil. Voucher specimens, M.G.Santos

* Corresponding author: E-mail: adrianapassos@pharma.ufrj.br (Adriana P. Oliveira)

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2253 (RFFP 17.338) and M.G. Santos 2191 (RFFP 14.491), respectively were deposited at the Herbarium of the Faculdade de Formação de Professores, Universidade do Estado do Rio de Janeiro, Brazil. The leaves of *Myrsine gardneriana* A.DC. were collected in April 2014 in Serra dos Órgãos National Park, Rio de Janeiro, Brazil and were identified by Dr. Maria de Fátima Freitas. A voucher specimen was deposited at the herbarium of the Instituto de Pesquisas Jardim Botânico do Rio de Janeiro, under the registration M.F. Freitas 415 (RB 606166).

2. Previous Studies

Primulaceae is a pantropical family and comprises 68 genera and 2.788 species [1]. The family is represented by 11 genera and 140 species in Brazil [2]. The species of Primulaceae present different types of secretory structures: idioblasts, glandular trichomes, and secretory cavities and glandular trichomes [3-5]. The tissues in Primulaceae synthesize hydroxybenzoquinone derivatives, with variable composition among species. Such compounds can be used as a chemotaxonomic character for genus segregation [6-7].

The genus *Myrsine*, popularly known as "capororoca" or "pororoca", belongs to the subfamily Myrsinoideae (Primulaceae), consists of trees, shrubs or subshrubs, usually presents secretory cavities as long as the whole plant and trichomes on leaves and flowers [8]. Despite the taxonomic importance, very little is known about the volatile constituents of the genus *Myrsine*, and only five species, *M. coriacea* (Sw.) R.Br. ex Roem. & Schult., *M. venosa* A. DC., *M. lessertiana* A.DC., *M. sandwicensis* A.DC. and *M. africana* L., have been reported on the chemical composition of essential oil [5,9]. Therefore, this study aims to analyse the volatile constituents of three Brazilian *Myrsine* species, the endemic *Myrsine rubra* and the natives *Myrsine gardneriana* and *Myrsine parvifolia*.

3. Present Study

In the present work, *Myrsine* (*M. parvifolia*, *M. rubra* and *M. gardneriana*) were collected at different locations in Rio de Janeiro State, Brazil. The chemical constituents of the essential oil of these three *Myrsine* species were identified by using GC-FID-MS analyses on the basis of their mass spectra, retention indices, literature data and the mass spectral libraries NIST [10-12]. The percentage of each component within the essential oils was determined on RTX-5 column and is presented in Table 1.

Essential oils of the three *Myrsine* species have a pale yellow color and characteristic pleasant odors with the yields (w/w) of 0.03% for *M. parvifolia*, 0.03% for *M. rubra*, 0.01% for *M. gardneriana* leaves and 0.01% for *M. parvifolia* fruits. A total of eighteen, thirteen, thirty one and thirty five compounds, were identified in the essential oils of *M. parvifolia*, *M. rubra* and *M. gardneriana* leaves and *M. parvifolia* fruits, accounting for 89.9%, 81.5%, 95.3% and 86.7%, respectively.

Major essential oil compounds of *M. parvifolia* were caryophyllene oxide (14.4%), β-caryophyllene (12.6%) and γ-Muurolene (7.9%) in the leaves oil, while the fruit oil consisted of β-caryophyllene (11.7%) and δ-Cadinene (7.1%). The main identified compounds were β-caryophyllene (17.2%), γ-Muurolene (11.1%) and Germacrene B (10.0%) for *M. rubra* and, β-caryophyllene (18.0%), γ-Muurolene (8.4%) for *M. gardneriana* leaves.

The essential oils from the *M. parvifolia* leaves, the *M. rubra* leaves, *M. gardneriana* leaves and the *M. parvifolia* fruits were characterized by the presence of sesquiterpenes, 89.9%, 81.5%, 95.3% and 86.0%, respectively. Previous studies on leaf essential oils of *M. coriacea*, *M. venosa*, *M. lessertiana*, *M. sandwicensis*, have been reported and similar data were found in their chemical compositions, as all of them were dominated by sesquiterpenes [5,13]. On the other hand, monoterpenes (α-pinene and β-pinene) were observed only in the oil from *M. parvifolia* fruits as can be seen from Table 1 and others monoterpenes (limonene, myrcene) were found as minor components in *M. sandwicensis* [13].

α-Humulene (5.0-6.3%), γ-muurolene (3.7-11.1%), β-selinene (1.3-6.7%), δ-cadinene (2.3-7.1%) and β-caryophyllene (11.7-18.0%) were detected in all oil samples, which were also identified in the essential oils from *M. coriacea* and *M. venosa* leaves [5] and *M. lessertiana* [13], although these compounds were not identified in the essential oil from *M. africana* fruits [9]. As can be observed from our findings, as well as from other analysis on essential oil from *Myrsin*e species [5,9,13], there is a notable tendency of those plants to biosynthesize sesquiterpenes.

Table 1. Relative abundance (%) of the chemical composition essential oils of *Myrsin*e species.

Compounds	**RI_{Lit}**	**RI_{Exp}**	***M. parvifolia* leaves[b]**	***M. rubra* leaves[b]**	***M. gardneriana* leaves[b]**	***M. parvifolia* fruits[b]**
α-pinene	932	935	-	-	-	0.4
β-pinene	974	979	-	-	-	0.3
α-Ylangene	1373	1375	2.4	-	1.6	0.5
α-copaene	1374	1379	-	-	3.9	6.0
Longifolene	1407	1410	-	-	-	0.4
β-caryophyllene	1417	1412	12.6	17.2	18.0	11.7
γ-elemene	1434	1427	-	3.2	-	-
Aromadendrene	1439	1443	-	-	3.0	-
β-Barbatene	1440	1439	-	2.1	-	0.6
Guaia-6,9-diene	1442	1437	1.6	-	-	1.1
α-Himachalene	1449	1443	2.5	-	-	6.1
α-Humulene	1452	1448	6.1	6.3	5.4	5.0
Clovene	1452	1462	1.4	-	-	-
Geranyl acetone	1453	1456	-	-	0.5	-
Alloaromadendrene	1458	1453	-	-	1.6	-
(E)-β-Caryophyllene	1464	1466	-	-	1.0	-
γ-Muurolene	1478	1481	7.9	11.1	8.4	3.7
γ -Himachalene	1481	1483	-	-	-	5.1
α-Amorphene	1483	1484	-	-	1.4	-
β-Selinene	1489	1491	6.7	6.4	1.3	2.7
γ-Selinene	1492	1495	-	-	-	1.2
γ-Amorphene	1495	1499	-	-	1.7	-
α-Selinene	1498	1499	5.9	5.3	-	4.0
α-Muurolene	1500	1505	-	1.2	1.3	-
β-Himachalene	1500	1505	4.5	-	-	5.9
γ-Cadinene	1513	1506	1.6	3.4	3.9	-
γ -Bisabolene	1514	1507	-	-	-	2.0
δ-Cadinene	1522	1512	2.3	3.9	3.9	7.1
Zonarene	1528	1529	6.3	-	-	-
γ -Dehydro-ar-himachalene	1530	1533	-	-	-	1.6
γ-Vetivenene	1531	1542	-	-	-	0.8
α-Cadinene	1537	1542	-	-	0,9	-
α-Calacorene	1544	1548	-	-	-	3.7
Selina-3,7(11)-diene	1545	1540	3.9	2.9	-	1.4
Germacrene B	1559	1554	-	10.0	-	-

Longicamphenylone	1562	1558	-	-	1.1	-
β-Calacorene	1564	1548	-	-	1.2	-
Caryophyllenyl alcohol	1570	1575	-	-	1.0	0.8
Caryophyllene oxide	1582	1588	14.4	8.5	-	2.1
Dihydromayurone	1595	1589	-	-	5.7	-
Cubeban-11-ol	1595	1600	-	-	2.3	-
Rosifoliol	1600	1607	-	-	0.4	-
Humulene epoxide II	1608	1603	3.9	-	1.9	-
Naphthalenemethanol	1622	1620	-	-	-	0.6
Isolongifolanone	1625	1629	-	-	7.5	-
Eremoligenol	1629	1622	3.0	-	-	-
Muurola-4,10(14)-dien-1-β–ol	1630	1634	-	-	-	1.5
cis-Cadin-4-en-7-ol	1635	1639	-	-	3.8	-
epi-Cadinol	1638	1631	-	-	-	0.9
Caryophylladienol II	1639	1642	-	-	1.8	1.0
T-Muurolol	1640	1648	-	-	0.9	-
Torreyol	1644	1652	-	-	1.4	-
Cubenol	1645	1638	-	-	-	0.9
α-Cadinol	1652	1647	-	-	-	1.1
Himachalol	1652	1649	2.9	-	-	1.3
Gymnomitrol	1658	1663	-	-	-	1.1
14-Hydroxiisocaryophyllene	1668	1672	-	-	6.1	0.7
α -Santalol	1674	1676	-	-	-	0.9
Cadalene	1675	1680	-	-	0.4	2.5
Khusilol	1679	1677	-	-	2.0	-
Sesquiterpenes: total			89.9	81.5	95.3	86.0
Monoterpenes: total			0	0	0	0.7
Total identified			89.9	81.5	95.3	86.7

RI_{Exp}: Retention index calculated from retention times relative to that of n-alkanes(C6-C32) on RTX-5 column. $RI_{Lit:}$ Retention index from literature [12]. [b]Percentages obtained by FID peak-area normalization.

This study presents the first report of the volatile constituents of *M. rubra*, *M. gardneriana*, *M. parvifolia*. Furthermore, the compounds longifolene, β-barbatene, α-himachalene, clovene, geranylacetone, γ-himachalene, γ-selinene, β-himachalene, γ-bisabolene, zonarene, γ -Dehydro-ar-himachalene, γ-vetivenene, longicamphenylone, β-calacorene, caryophyllenyl alcohol, dihydromayurone, cubeban-11-ol, rosifoliol, naphthalenemethanol, isolongifolanone, eremoligenol, epi-Cadinol, muurola-4,10(14)-dien-1-β–ol, cis-Cadin-4-en-7-ol, caryophylladienol II, torreyol, himachalol, gymnomitrol, 14-hydroxiisocaryophyllene, α-santalol, cadalene and khusilol were not previously recorded in the genus.

SØrenses's similarity index and Unweighted Pair Group Method with Arithmetic Mean (UPGMA) clustering were used to compare the essential oil compositions between data available on Primulaceae species [5, 9, 13-17] The dendrogram shows (Figure 1) that all *Myrsine* species formed a cluster, with the exception of *Myrsine africana*, which was very different of all Primulaceae species and did not group with the other species. Highest similarity was reserved for *Myrsine parvifolia* leaves and *M. rubra* leaves (58%), followed by *Myrsine coriacea* leaves and *M. lessertiana* leaves (50%); *Myrsine venosa* leaves and *M. lineata* leaves (43%).

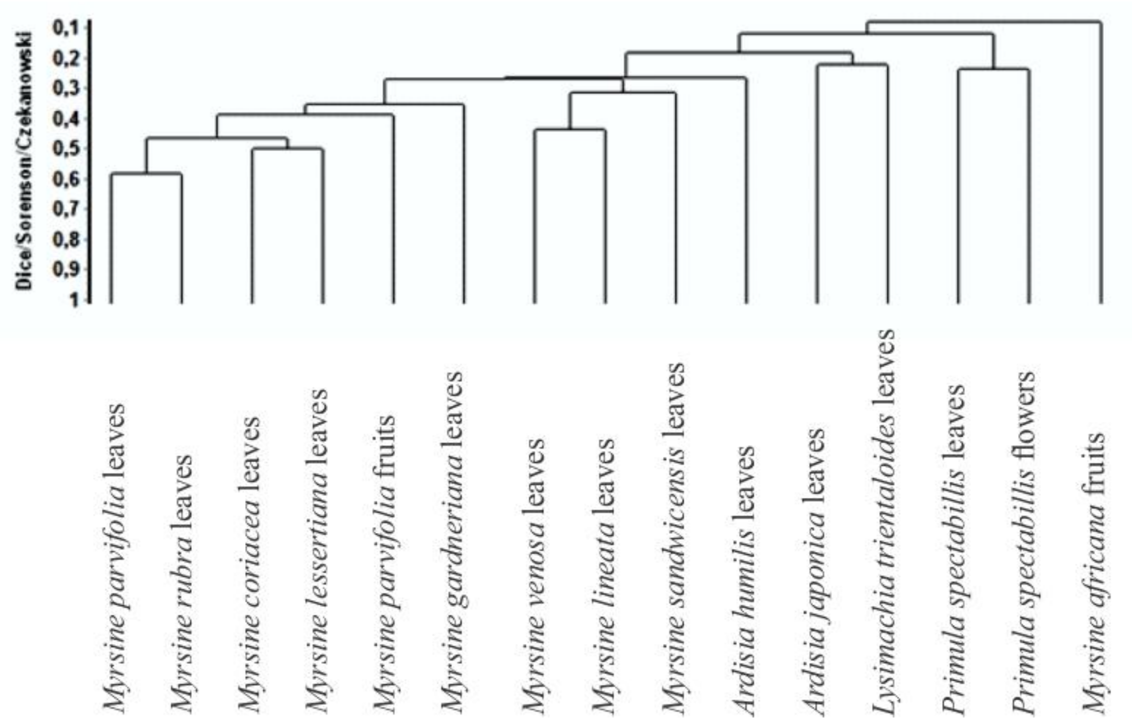

Figure 1. Dendrogram of the similarity following SØrenses's index of the essential oil composition between Primulaceae species. Cophenetic correlation: 0.8741. Literature data [5, 9, 13-17].

The knowledge of the occurrence and the evolution process of these metabolites compounds may be helpful in further studies of ecology and phylogenetic of Primulaceae, especially among *Myrsine* species. The present data are a new study that could be used in enriching our current knowldege about *Myrsine* genus.

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Supporting Information

Supporting Information accompanies this paper on http://www.acgpubs.org/RNP

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