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VOLATILE COMPOUNDS FROM LEAVES AND FLOWERS OF *Garcinia macrophylla*

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The genus *Garcinia* (Clusiaceae = Guttiferae) consists of roughly 260 species of dioecious trees and shrubs distributed in South America (where they are also known under the synonym *Rheedia*), Africa, Madagascar, and Southeast Asia. *Garcinia macrophylla* Mart. (*Rheedia macrophylla* (Mart.) Planch. & Triana) is a tree growing to 20 m tall native to the Amazonian region and the Atlantic rainforest in Brazil, where it is commonly known as "bacuri", "bacupari", "bacopare", and "bacupari-verdadeiro". Part of these popular names are also used for a closely related species, *Garcinia gardneriana* (Planch. & Triana) Zappi (*Rheedia gardneriana* Planch. & Triana) [1]. The mesocarp of the yellow fruits is edible and has a pleasant acidic flavor, for which reason the species is locally cultivated in the Amazon. The yellow resin exuded from bark and fruits is used in Brazilian folk medicine to treat swelling and injury [2, 3]. Although several phytochemical studies on *Garcinia gardneriana* have been published [4–9], up to now only one phytochemical study is known on *G. macrophylla* [10] and there are no previous reports on the essential oil composition from this species. The aim of this work was to analyze the chemical composition of the essential oils from the leaves and flowers of *G. macrophylla* growing in the Atlantic forest in northeast Brazil. To the best of our knowledge, this is the first report on the chemical composition of essential oils from this species.

In this present study, the composition of the volatile oils from the leaves and flowers of *Garcinia macrophylla* obtained by hydrodistillation was analyzed by GC/MS. The results are shown in Table 1. Thus, it was possible to identify twenty-eight components in the oil extracted from flowers, representing 93.7% of the total oil with 60.8% oxygen-containing monoterpenes, 20.2% oxygen-containing sesquiterpenes, 9.1% fatty acid derivatives, 3.6% benzenoids, and 4.4% unidentified compounds. The seven major components identified (representing 73.2% of the oil) were (*Z*)-linalool oxide (4.1%), (*E*)-linalool oxide (4.5%), linalool (13.3%), hotrienol (24.8%), phenyl ethanol (2.5%), pinocampheol (8.7%), and selin-11-en-4α-ol (15.3%). In the oil from leaves we identified forty-seven compounds, representing 96.6% of the total oil with predominance of sesquiterpene hydrocarbons (69.3%) and fatty acid derivatives (22.6%) besides minor percentages of oxygen-containing sesquiterpenes (3.7%) and benzenoids compounds (1.0%). The eight major constituents identified (representing 77.5% of the oil) were (*Z*)-3-hexen-1-ol (14.7%), 1-hexanol (3.2%), α-copaene (16.2%), β-caryophyllene (18.0%), α-humulene (4.0%), alloaromadendrene (9.0%), γ-cadinene (8.8%), and δ-cadinene (3.6%).

As expected, the volatile composition of the leaves and flowers of *G. macrophylla* showed differences both qualitatively and quantitatively regarding the proportions of the major components. There are similarities to the volatile profiles of some other Clusiaceae like *Kielmeyera rugosa* Choisy [11]. One can observe differences in the proportions of the main components, however, when comparing the relative percentages of volatile compounds from flowers of *G. macrophylla* (oxygen-containing monoterpenes 60.8%, oxygen-containing sesquiterpenes 20.2%, fatty acid derivatives 9.1%, benzenoids compounds 3.6%) with those obtained from other Clusiaceae species [11, 12]. Thus, oxygen-containing monoterpenes (60.8%) are the major compounds in the flowers of *G. macrophylla*, while benzenoid compounds (94.5%) and sesquiterpenes hydrocarbons (88.5%) are predominant in the flowers of *Kielmeyera rugosa* and *Mesua ferrea*, respectively [11, 13].

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TABLE 1. Volatile Composition of the Leaves and Flowers of Garcinia macrophylla[a]

Compound	RI[b] (calc.)	RI[c] (lit.)	Peak area, %		Compound	RI[b] (calc.)	RI[c] (lit.)	Peak area, %	
			leaves	flowers				leaves	flowers
Ethyl propanoate	726	714	Tr.	-	β-Bourbonene	1386	1384	0.7	-
n-Propyl acetate	728	-	Tr.	1.0	β-Caryophyllene	1423	1419	18.0	-
Isobutyl acetate	754	776[d]	0.2	-	β-Gurjunene	1430	1432	0.3	-
1-Hexanal	807	800	1.1	-	α-*trans*-Bergamotene	1435	1436	0.7	-
2-Hexanal	850	854[d]	0.9	-	Aromadendrene	1440	1439	1.1	-
(*E*)-3-Hexen-1-ol	851	851	0.3	-	α-Himachalene	1448	1447	0.4	-
(*Z*)-3-Hexen-1-ol	855	857	14.7	-	α-Humulene	1454	1454	4.0	-
1-Hexanol	866	867	3.2	-	Alloaromadendrene	1461	1461	9.0	-
Hexanoic acid	991	981[e]	0.9	1.3	γ-Muurolene	1474	1477	1.9	-
(*E*)-3-Hexenoic acid	1011	-	0.3	-	Germacrene D	1477	1480	0.2	-
2-Ethyl hexanol	1025	1032[d]	0.3	1.2	β-Selinene	1486	1485	1.1	-
Benzeneacetaldehyde	1040	1043	-	1.1	Viridiflorene	1486	1493	0.2	-
Ethyl 2-furoate	1050	-	0.2	-	α-Selinene	1492	1494	1.7	-
(*E*)-2-Octenal	1055	1060[d]	0.5	-	α-Muurolene	1502	1499	0.7	-
Acetophenone	1062	1065	0.2	-	γ-Cadinene	1517	1513	8.8	-
(*Z*)-2-Octen-1-ol	1067	-	-	1.4	δ-Cadinene	1525	1524	3.6	-
(*Z*)-Linalool oxide	1070	1074	-	4.1	Cadina-1,4-diene	1532	1532	0.3	-
(*E*)-Linalool oxide	1086	1088	-	4.5	α-Cadinene	1538	1538	0.20	-
Linalool	1098	1098	Tr.	13.3	α-Calacorene	1543	1542	0.2	-
n-Nonanal	1102	1098	Tr.	-	(*E*)-Nerolidol	1559	1564	Tr.	-
Hotrienol	1103	1101[d]	-	24.8	(*Z*)-3-Hexenyl benzoate	1566	1570	Tr.	-
Phenyl ethanol	1109	1110	-	2.5	Spathulenol	1574	1576	0.3	0.3
Benzeneacetonitrile	1134	1135[e]	-	Tr.	Caryophyllene alcohol	1575	1568	-	Tr.
Nerol oxide	1153	1153	-	1.1	Caryophyllene oxide	1582	1581	1.7	-
(*E*)-2-Nonenal	1158	1162[d]	-	1.3	Globulol	1589	1583	0.2	1.4
Pinocampheol	1168	1170	-	8.7	NI	1606	-	-	0.8
(*Z*)-3-Hexenyl butyrate	1188	1186	-	0.3	NI	1618	-	-	0.9
α-Terpineol	1190	1189	-	1.9	1-*epi*-Cubenol	1630	1627	0.3	0.8
Methyl salicylate	1192	1190	0.8	-	*epi*-α-Muurolol	1643	1641	0.4	1.4
NI	1222	-	-	1.0	α-Muurolol	1645	1645	Tr.	1.0
Nerol	1228	1228	-	0.5	α-Cadinol	1656	1653	0.5	-
Geraniol	1254	1255	-	1.1	Selin-11-en-4α-ol	1660	1652	-	15.3
NI	1290	-	-	1.0	NI	1665	-	-	0.7
(2*E*,4*E*)-Deca-2,4-dienal	1315	1314	-	0.4	14-Hydroxy-9-*epi*-β-caryophyllene	1670	1664	0.3	-
3,7-Dimethyl-1,5-octadien-3,7-diol	1357	-	-	0.8	Isopropyl miristate	1826	-	-	2.2
α-Copaene	1378	1376	16.2	-	Total			96.6	98.1

[a]Tr.: traces (mean value below 0.1%); [b]RI (calc.), retention index on DB-5 column; NI, compounds not identified; [c]RI (lit.), retention index according to [15]; [d]retention index according to [16]; [e]RI (lit.), retention index according to [12].

Furthermore, no *Clusia* species studied by Nogueira et al. [12] has a volatile chemical profile similar to *G. macrophylla*. It is noteworthy that *Clusia* and *Garcinia* are phylogenetically closer, both belonging to the subfamily Clusioideae, while *Mesua* and *Kielmeyera* belong to the subfamily Kielmeyeroideae. So far as is known, bees are the most important pollinators of the flowers of *Mesua* as well as of the neotropical representatives of *Clusia*, *Garcinia*, and *Kielmeyera*. These results suggest that the evolution of the flower fragrances is too rapid to allow for useful comparisons at the generic level. This is probably due to the selection pressure caused by the necessary adaptation to the pollinators occurring in the distribution area of a particular species. Thus comparisons of floral volatiles are more interesting at the specific level as was demonstrated for the genus *Clusia* by Nogueira et al. [12]. Volatiles of other plant parts, on the other hand, seem to evolve so slowly that they are not even useful

markers at the subfamilial level. These results represent the first reported case, at the moment, on the volatile compounds of *Garcinia macrophylla*.

Plant Material and Isolation of the Essential Oils. Leaves and flowers of *Garcinia macrophylla* were collected in the proximity of the "Vaza Barris" River in the Municipality of Itaporanga D'ajuda, Sergipe state, Brazil. A voucher specimen (M. C. E. Amaral, V. Bittrich, A. S. Ribeiro, and P. C. L. Nogueira #239) has been deposited in the herbarium LEEP/UFS. The essential oils from fresh flowers (6.9 g in 50 mL water) and leaves (92.0 g in 1200 mL water) were obtained in November/2002 by hydrodistillation for 3 h, using a Clevenger type apparatus. The volatile compounds were extracted from the distillation water with dichloromethane, dried over anhydrous sodium sulfate, and carefully concentrated under N_2 to a final volume <0.5mL. The samples were stored in sealed glass vials in a refrigerator at 4–5°C prior to analysis.

Analysis of Essential Oils (GC/MS analysis). Analyses were carried out using a Shimadzu QP5050A system equipped with a J&W Scientific DB-5 fused silica capillary column (30m × 0.25mm i.d. × 0.25 μm film thickness); column temperatures were programmed from 40°C for 2 min, raised to 220°C at 4°C/min, then to 280°C at 20°C/min. Injector and detector temperatures were 250°C and 280°C, respectively. Helium was used as carrier gas, with flow rate 1.5 mL/min, split mode. Injection volume was 1.5 μL solution in ethyl acetate. The MS were taken at 70 eV. Scanning speed was 0.5 scan/sec from *m/z* 40 to 550. The retention indices were obtained by co-injecting the oil sample with a C_{10}–C_{24} linear hydrocarbon mixture (retention index from 700 to 999 was obtained by extrapolation). The percent composition of each component was determined from the area of the component divided by the total area of all components isolated under these conditions.

The volatile components were analyzed by GC/MS, and identification was made by comparison of retention indices [14] as well as by computerized matching of the acquired mass spectra with those stored in the NIST mass spectral library of the GC/MS data system and other published mass spectra [15].

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