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Article

3-Ishwarone and 3-Ishwarol, Rare Sesquiterpenes in Essential Oil from Leaves of *Peperomia oreophila* Hensch.

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O óleo essencial obtido das folhas de *Peperomia oreophila* (Piperaceae) foi submetido a fracionamento em gel de sílica. Esse processo de separação resultou em uma fração composta por uma mistura de hidrocarbonetos sesquiterpênicos que foram identificados como β-elemeno, α-ilangeno, α-guaieno e β-selineno. Além desses, também foram identificados o espatulenol e dois sesquiterpenos com raro esqueleto ishwarano: o 3-ishwarol e a 3-ishwarona, sendo esta última, o componente majoritário do óleo bruto (78% em massa). Uma vez que o álcool foi obtido em quantidade insuficiente para caracterização estrutural, maiores quantidades foram obtidas por meio da redução da cetona original. Os dois sesquiterpenos foram purificados e depois caracterizados por meio de técnicas espectrométricas (^{1}H-^{1}H COSY, HMQC, HMBC e NOESY).

The essential oil from *Peperomia oreophila* leaves (Piperaceae) was submitted to fractionation in silica gel column. This separation procedure yielded a fraction composed of a hydrocarbon sesquiterpene mixture which was identified as β-elemene, α-ylangene, α-guaiene and β-selinene. Besides, spathulenol and two sesquiterpenes with the rare ishwarane skeleton: 3-ishwarol and 3-ishwarone were also identified. 3-ishwarone was the major component of the crude oil (78% weight). Since the alcohol obtained was not sufficient to allow a complete structural determination, the original ketone was reduced to 3-ishwarol in order to give additional quantities. After the two sesquiterpenes purification, they were characterized by spectrometric techniques (^{1}H-^{1}H COSY, HMQC, HMBC and NOESY).

Keywords: *Peperomia oreophila*, essential oil, ishwarane sesquiterpenes, 3-ishwarol, 3-ishwarone

Introduction

As part of our ongoing phytochemical research on Brazilian Piperaceae species, we have investigated extracts from *Piper* and *Peperomia* species.[1-4] The genus *Peperomia* has over 1000 species occurring in the tropics, its leaves have a variety of size and shape and are adapted to moist habitat and dry highlands as well. In despite of the large number of *Peperomia* species, only a few species have been chemically analyzed and, as a result, amides, chromenes, benzoic acids, lignoids and poliketide derivatives were isolated.[5-7] Furthermore, there is only one report on the chemical composition of volatile compounds in *Peperomia* species, in which phenylpropanoids were identified in *P. subespatulata*.[8]

In this paper, we report the chemical study of essential oil from leaves of *P. oreophila*, including the isolation and structural determination of two sesquiterpenes with a rare skeleton, 3-ishwarol and 3-ishwarone. Despite these sesquiterpenes have previously been described as synthetic products,[9] in the present article, we describe their first occurrence as natural products. Additionally, complete assignments of the spectral data to 3-ishwarol and 3-ishwarone were performed including 2D NMR (^{1}H-^{1}H COSY, HMQC, HMBC and NOESY) analyses.

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Results and Discussion

P. oreophila leaves essential oil was analyzed by gas chromatography (GC) and submitted to separation on silica gel column affording 8 fractions that were individually analyzed with GC. Fractions 1 and 2, composed by hydrocarbon sesquiterpenes, were pooled and analyzed with GC/MS, allowing the identification of β-elemene (**1**), α-ylangene (**2**), α-guaiene (**3**) and β-selinene (**4**). Fraction 7 was constituted by spathulenol (**6**) according to its NMR spectra.[10,11]

Fraction 5, after purification procedures, yielded the sesquiterpene **5** whose structure was deduced from the IR, MS, and NMR spectral data. The IR spectrum exhibited a strong absorption at 1680 cm^{-1}, indicating the presence of a carbonyl group in its molecular structure. The molecular formula $C_{15}H_{22}O$ was determined with analysis of LREIMS ($[M]^+$ *m/z* 218) and ^{13}C NMR (BBD and DEPT 135°) spectral data, which displayed fifteen signals referring to three methyls, five methylenes, three methines, as well as four quaternary carbons, among which one of carbonyl group. The hydrogen deficiency index to **5** was calculated as five, which in association to the absence of olefinic carbons and the presence of a carbonyl group, suggest a tetracyclic molecule, a quite unusual feature for a sesquiterpene skeleton.

Inspection of NMR data indicated several similar signals to those of ishwarane derivatives, such as 1-methyl-10-oxo-tetracyclo [7.2.1.$0^{2,11}$.$0^{4,9}$] dodecane, 8-ishwarone, 8-ishwarol, and ishwarane which possess four rings in their structures.[12,13] These similarity associated to the knowledge of the occurrence of ishwarane sesquiterpenoids in *Piper alamago*,[12] a Piperaceae species, provided the basis for its determination.

Since the ^1H NMR spectrum in $CDCl_3$ showed several overlapped signals at δ 1.0-2.5, this spectrum was recorded in C_6D_6 (Table 1). Thus, three methyl groups splitted apart into two quarternary methyl groups at d 0.89 (s, 3H), 0.96 (s, 3H) and a secondary one at δ 1.25 (d, *J* 6.6 Hz, 3H) were observed. By using HMQC and HMBC techniques, ^1H and ^{13}C signals could be assigned (Table 1). The HMQC spectrum showed the hydrogen bearing carbons in structure of **5** which, in association to ^1H-^1H COSY spectrum, positioned the carbonyl group at C-3. The HMBC long range correlation between H-1 and C-3, C-9, C-10, C-12, between H-13 and C-1, C-2, C-10, C-11 and between H-12 and C-2, C-4, C-9, C-10 and C-11 determined the partial tricycle moiety of ishwarane skeleton and confirmed the carbonyl group at C-3. These assignments could also be confirmed based on the shielding (γ effect) observed to C-14 methyl group (δ_C 12.0) which only would be possible when carbonyl group is linked at C-3. Correlation between H-7 and C-5, C-9, between H-14 and C-3, C-4, C-5, C-9 and between H-5 and C-4, C-6, C-7, C-9, C-14 and C-15 completed the structural elucidation of this derivative. Thus, based on

Table 1. NMR data for 3-ishwarone (**5**) (500 and 125 MHz, δ, C_6D_6)

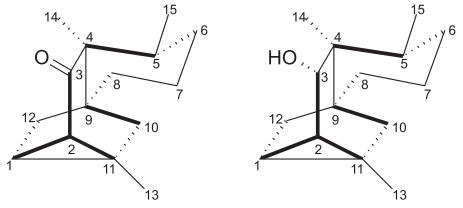
	^1H (multiplicity, *J*/Hz)	^1H-^1H COSY*	NOESY	^{13}C	HMBC (H→C)
1	1.14 (dd, 7.4, 2.8)	H-2, H-12b	-	29.9 (CH)	C-3, C-9, C-10, C-12
2	1.53 (d, 7.4)	H-1	H-13	37.9 (CH)	C-4, C-10, C-12, C-13
3	-	-	-	213.4 (C)	-
4	-	-	-	49.9 (C)	-
5	1.76 (dqd, 12.1, 6.6, 4.0)	H-6a, H-6b, H-15	H-6b, H-10b, H-15	31.8 (CH)	C-4, C-6, C-7, C-9, C-14, C-15
6	a: 1.02 (m) b: 1.23 (m)	H-5, H-6b, H-7a, H-7b H-5, H-6a, H-7a, H-7b	H-6b	31.5 (CH_2)	C-4, C-5, C-8, C-15C-4, C-5, C-8, C-15
7	a: 1.14 (m) b: 1.32 (m)	H-6a, H-6b, H-7b, H-8a, H-8b H-6a, H-6b, H-7a, H-8a, H-8b	H-7b, H-8a H-7a	23.6 (CH_2)	C-5, C-9C-5, C-9
8	a: 0.89 (m) b: 1.33 (m)	H-7a, H-7b, H-8b H-7a, H-7b, H-8a	H-7a, H-8b, H-14 H-8a	32.2 (CH_2)	C-4, C-6, C-7, C-9, C-10, C-12 C-4, C-6, C-7, C-9, C-10, C-12
9	-	-	-	43.1 (C)	-
10	a: 1.98 (d, 12.4) b: 0.97 (d, 12.4)	H-10a H-10b	H-5, H-10b H-10a	39.5 (CH_2)	C-2, C-4, C-9, C-11, C-12 C-2, C-4, C-9, C-11, C-12
11	-	-	-	30.0 (C)	-
12	a: 1.65 (d, 12.4) b: 1.10 (dd, 12.4; 2.8)	H-12b H-1, H-12a	H-12b, H-14 H-12a	35.1 (CH_2)	C-2, C-4, C-9, C-10, C-11 C-2, C-4, C-9, C-10, C-11
13	0.96 (s)	-	H-2	19.5 (CH_3)	C-1, C-2, C-10, C-11
14	0.89 (s)	-	H-8a, H-12a	12.0 (CH_3)	C-3, C-4, C-5, C-9
15	1.25 (d, 6.6)	H-5	H-5	17.7 (CH_3)	C-4, C-5, C-6

*registered in $CDCl_3$.

the above evidence, the structure of **5** was established as 3-ishwarone.

The ^{1}H NMR spectrum of purified fraction 7 (C_6D_6) showed three methyl groups at δ 0.89 (d, J = 6.6 Hz), 0.74 (s), 1.12 (s) and several signals at δ 0.5 – 2.0, similar to those observed to 3-ishwarone. However, the triplet at δ 1.53 (J = 7.4 Hz), assigned to α-carbonyl hydrogen H-2, was not observed but a broad singlet at δ 3.66 (1H) instead, suggesting the presence of an alcohol derivative (**7**). As the amount of this compound was not sufficient to determine the structure, it was produced by reduction of ketone derivative (**5**), followed by GC, GC/MS, IR and NMR analysis. Therefore, compound **5** (35 mg) was treated with $NaBH_4$ in THF/MeOH to afford the sesquiterpene **7** (35 mg). Analysis of the IR spectrum with a broad band at ν_{max} 3373 cm^{-1} (hydroxyl group) in association to LREIMS, which showed the molecular ion-peak at *m/z* 220 Da, compatible with molecular formula $C_{15}H_{24}O$, was indicative of the successful of this reduction reaction. The ^{1}H NMR spectrum (C_6D_6) of **7** was identical to that observed previously to the alcohol derivative isolated from the essential oil indicating the same structure to these two compounds. The ^{13}C NMR spectrum of **7** (BBD and DEPT 135°) showed 15 signals in which three methyl groups (δ 20.2, 16.7 and 9.0), five methylene groups (δ 38.9, 35.7, 33.9, 30.7 and 24.2), four methine groups (δ 73.9, 38.6, 28.4 and 23.0) and three quaternary carbons (δ 43.5, 41.4 and 22.4). As suggested previously, the occurrence of an oxygenated sesquiterpene was confirmed by the signal at δ 73.9 (CH) assigned to carbinolic C-3. The hydrogen bearing carbon signals were assigned by HMQC spectrum and showed cross-peak between C-3 and H-3 at δ 3.66 (broad singlet). HMBC spectrum showed correlations between H-3 and C-1, C-5, C-9, C-11 and C-14, thus confirming the structure of 3-ishwarol. In order to determine the relative stereochemistry of C-3, the NOESY spectrum of **7** was recorded (Table 2) which showed cross-peaks between H-3 and H-5, H-10a and H-15, between H-14 and H-8a, H-12a and between H-5 and H-10a, H-3. Therefore, the relative configuration of C-3 was determined as R*. Finally, the co-injection of the synthetic 3-ishwarol with that isolated from the crude oil provided conclusive evidence to confirm the structure of natural sesquiterpene **7**.

Thus, after characterization of compounds **5** and **7** with NMR techniques, the main compounds of the crude essential oil from leaves of *Peperomia oreophila* were identified as showed in Table 3.



5 **7**

The occurrence of 3-ishwarone as major derivative in *P. oreophila* leaves crude oil was detected using NMR experiments, before chromatographic procedures. As these data suggested the occurrence of an unusual compound in essential oils, the chromatographic separation was

Table 2. NMR data for 3-ishwarol (**7**) (500 and 125 MHz, δ, C_6D_6)

	^{1}H (multiplicity, *J*/Hz)	^{1}H-^{1}H COSY	NOESY	^{13}C	HMBC (H→C)
1	0.82 (dd, 7.1, 2.9)	H-2, H-12b	H-2	23.0 (CH)	C-3, C-9, C-10, C-12, C-13
2	0.56 (d, 7.1)	H-3	H-1, H-3, H-13	28.4 (CH)	C-4, C-10, C-12, C-13
3	3.66 (sl)	H-2	H-2, H-5, H-10a, H-15	73.9 (CH)	C-1, C-5, C-9, C-11, C-14
4	-	-	-	41.4 (C)	-
5	1.33 (m)	H-6a, H-6b, H-15	H-3, H-10a, H-15	38.6 (CH)	C-3, C-4, C-6, C-7, C-14, C-15
6	a: 1.21 (m)	H-5, H-6b, H-7a, H-7b	H-6b	30.7 (CH_2)	C-4, C-5, C-7, C-8, C-15
	b: 1.04 (dd, 12.0; 3.9)	H-5, H-6a, H-7a, H-7b			C-4, C-5, C-7, C-8, C-15
7	a: 1.38 (m)	H-6a, H-6b, H-7b, H-8a, H-8b	H-8b	24.2 (CH_2)	C-5, C-6, C-8, C-9
	b: 1.26 (m)	H-6a, H-6b, H-7a, H-8a, H-8b			C-5, C-6, C-8, C-9
8	a: 1.51 (m)	H-7a, H-7b, H-8b	H-8b, H-14	33.9 (CH_2)	C-6, C-7, C-9, C-10, C-12
	b: 0.95 (m)	H-7a, H-7b, H-8a	H-8a, H-7a		C-6, C-7, C-9, C-10, C-12
9	-	-	-	43.5 (C)	-
10	a: 1.89 (d, 12.0)	H-10b	H-3, H-5, H-10b	38.9 (CH_2)	C-2, C-4, C-8, C-9, C-11, C-12, C-13
	b: 0.87 (d, 12.0)	H-10a	H-10a		C-2, C-4, C-8, C-9, C-11, C-12, C-13
11	-	-	-	22.4 (C)	-
12	a: 1.79 (d, 12.0)	H-12b	H-12b, H-14	35.7 (CH_2)	C-1, C-2, C-4, C-8, C-9, C-10
	b: 1.12 (dd, 12.0; 2.7)	H-1, H-12a	H-12a		C-1, C-2, C-4, C-8, C-9, C-10
13	1.12 (s)	-	H-2	20.2 (CH_3)	C-2, C-10, C-11
14	0.74 (s)	-	H-8a, H-12a	9.0 (CH_3)	C-3, C-4, C-5, C-9
15	0.89 (d, 6.6)	H-5	H-3, H-5	16.7 (CH_3)	C-4, C-5, C-6

Table 3. Chemical composition of the essential oil from leaves of *P. oreophila*

component	RR_t/s	RI	percentage
β-elemene (**1**)	1170	1375	1.4
α-ylangene (**2**)	1212	1322	0.8
α-guaiene (**3**)	1284	1491	2.4
β-selinene (**4**)	1332	1608	0.8
3-ishwarone (**5**)	1674	1807	78.2
spathulenol (**6**)	1728	1825	2.6
3-ishwarol (**7**)	1926	2020	0.8
TOTAL			87.0

necessary to allow the identification of this compound, since it was not identified with GC/MS as well. Additionally, the spectrometric analysis of the fractions obtained with chromatographic separation of crude hexane extract showed the presence of 3-ishwarone, indicating that this compound occurs also in high amount in the apolar extract from leaves. Thus, the hypothesis of formation of this compound as artifact by hydrodistillation and/or chromatographic procedures must be discarded.

Sesquiterpenes containing the ishwarane skeleton are quite rare. These derivatives were detected previously only in Aristolochiaceae,[9,14-16] Annonaceae,[17] Bixaceae[18] and Piperaceae[12] species.

Experimental

General procedures

Silica gel (Merck, 230-400 mesh) was used for column chromatographic separations while silica gel 60 PF_{254} (Merck) was used for analytical (0.25 mm) and prepared. TLC (1.0 mm). Optical rotations were measured in a digital polarimeter JASCO DIP-370 (Na filter, λ = 588 nm). IR spectra were measured in KBr pellets and NaCl film in a Perkin-Elmer Infrared Spectrometer model 1750. LREIMS spectra were measured at 70 eV on a HP 5990/5988A spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz in a Brüker DRX-500 spectrometer. $CDCl_3$ and C_6D_6 (Aldrich) was used as solvent and TMS as internal standard. Chemical shifts were reported in δ units (ppm) and coupling constants (*J*) in Hz. GC data was obtained by a Hewlett-Packard 5890 series II equipped with FID detector and a capillary column HP-5, crosslinked 5% phenyl in methyl silicone (30 m × 0.32 mm; film tickness 0.25 mm), an automatic injector (HP 7673) and electronic integrator (HP 3396A) were used. The temperature programming started at 100 °C (2 min), 100-240 °C at 5 °C min^{-1}, then isothermal at 240 °C (5 min). The injector and detector temperatures were 180 °C and 260 °C, respectively, and helium was used as the carrier gas. Quantitative data was obtained from electronic integration of the area percent data without the use of and internal standard or correction factors. GC/MS analysis were carried out in as EIMS 70 eV Hewlet-Packard HP-5973 coupled with a Hewlet-Packard HP-6890 with DB-5 column (30 m × 0.25 mm, film tickness 0.25 mm) using the same temperature programming conditions above described. The identification of the compounds, except **5** and **7**, was performed by comparing the mass spectra and the retention index,[19] which were determined relatively to the retention time of a series of n-alkanes, with those of authentic samples.

Plant material

Peperomia oreophila Hensch. leaves were collected in Poços de Caldas, Minas Gerais, Brazil in May/2002. Plant material identification was performed by Dr. Elsie F. Guimarães. A voucher specimen (Kato-225) was deposited in the Herbarium of Instituto de Botânica, São Paulo, Brazil.

Extraction and isolation

The fresh leaves of *P. oreophila* (245 g) were subjected to hydrodistillation during four hours using a Clevenger-type apparatus to give 120.1 mg of yellow pale crude oil (~0.05%), which were immediately submitted to GC and GC/MS analysis. Part of this material (100.0 mg) was submitted to flash chromatography on silica gel eluted with CH_2Cl_2 (100 mL) and gradient of CH_2Cl_2-MeOH 95:5 (50 mL) and 9:1 (50 mL) to afford eight fractions (15 mL each) which were analyzed with gas chromatography.[20] Fraction 1 (10.2 mg), eluted with CH_2Cl_2, was subjected to analysis with GC/MS to allowed the identification of β-elemene, α-ylangene, α-guaiene and β-selinene. GC chromatograms of fractions 2-4 showed to be composed by complex mixtures of sesquiterpenes.[21] Fraction 5 (62.1 mg), eluted with CH_2Cl_2-MeOH 95:5, and 6 (9.0 mg), eluted with CH_2Cl_2-MeOH 9:1, showed GC chromatograms with intense peaks at RR_t = 1674 and 1926 seconds, respectively. Thus, these fractions were individually submitted to prep. TLC on Si-gel eluted with CH_2Cl_2 (twice) affording, respectively, **5** (46.3 mg) and **7** (0.5 mg). Fraction 7, eluted with CH_2Cl_2-MeOH 9:1, was composed of nearly pure spathulenol (3.1 mg).

Reduction of 3-ishwarone

To a stirred solution of **5** (35 mg, 0.16 mmol) in THF (5 mL) was added $NaBH_4$ (7.6 mg, 0.2 mmol) dissolved

in MeOH (1 mL). After 4 h, the reaction mixture was partitioned between EtOAc and saturated NaCl solution. The combined organic soluble solution was dried ($MgSO_4$) and evaporated *in vacuo* to afford 3-ishwarol **7** (35 mg, 99.4%) as a white amorphous solid, which was obtained without further purification.

*3-ishwarone (**5**)*

White amorphous solid. $[\alpha]_D^{30}$ +111.1° (*c* 0.35, $CHCl_3$). IR (KBr) ν_{max}/cm^{-1}: 3033 (cyclopropane ring), 2929 (C-H), 1680 (C=O), 1450, 1245, 899. LREIMS (70 eV) *m/z* (rel. int.) 218 $[M]^+$(17), 200(5), 190(8), 185(4), 175(6), 161(14), 147(29), 133(14), 119(40), 106(83), 93(100), 85(50), 77(39), 67(31), 55(84), 41(93). ^{1}H and ^{13}C NMR: see Table 1 (spectra recorded in C_6D_6).

*3-ishwarol (**7**)*

White amorphous solid. $[\alpha]_D^{30}$ –394.5° (*c* 0.26, $CHCl_3$). IR (film) ν_{max}/cm^{-1}: 3373 (OH), 2934 (cyclopropane ring), 2857 (C-H), 1675, 1384, 1004 (C-O), 932. LREIMS (70 eV) *m/z* (rel. int.): 220 $[M]^+$(10), 202(5), 192(4), 187(4), 177(2), 163(6), 145(7), 131(15), 118(100), 108(52), 105(40), 93(63), 91(33), 81(20), 79(20), 77(20), 69(12), 67(17), 55(34), 41(44). ^{1}H and ^{13}C NMR: see Table 2 (spectra recorded in C_6D_6).

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