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Eudesmanolides and other terpenoids from *Trattinickia rhoifolia*

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Resumen:

De la resina de *Trattinickia rhoifolia* fueron aisladas tres eudesmanolidas, 8*β*,9*α*-dihidroxieudesma-4(15),7(11)-dien-12,8-olida (**1**), 8*α*,9*α*-epoxieudesma-4(15),7(11)-dien-12,8-olida (**2**), y 8,8'-*bis*[eudesma-4(15),7(11)-dien-12,8*β*-olida] (**3**), y diecisiete compuestos conocidos. Las estructuras de los compuestos fueron elucidadas mediante la interpretación de los datos espectroscópicos y el análisis del modelaje molecular.

Palabras clave: *Trattinickia rhoifolia*; Burseraceae; Sesquiterpenoides; Eudesmano; Eudesmanolidas.

Abstract

Three eudesmanolides, 8*β*,9*α*-dihydroxyeudesma-4(15),7(11)-dien-12,8-olide (**1**), 8*α*,9*α*-epoxyeudesma-4(15), 7(11)-dien-12,8-olide (**2**), and 8,8'-*bis*[eudesma-4(15),7(11) -dien-12,8*β*-olide] (**3**), together with seventeen known compounds were isolated from the resin of *Trattinickia rhoifolia*. The structures of the compounds were elucidated by spectroscopic data interpretation and molecular modeling analysis.

Keywords: *Trattinickia rhoifolia*; Burseraceae; Sesquiterpenoids; Eudesmane; Eudesmanolides.

Introduction

Burseraceae is a family conformed by already 800 species partitioned in 18 genera distributed in 3 tribes (Burserae, Canariae y Protieae). The species from this family are characterized by exude aromatic oleoresins with prevalent therapeutic and liturgical uses (e.g. *Commiphora myrrha*, myrrh, and *Boswellia sp.*, incense). From phytochemical point of view, these oleoresins are mainly constituted by pentacyclic triterpenes and eudesmane sesquiterpenoids. The species of *Trattinickia* genus are controversially located in the Protieae tribe and is integrated by 21 species which are distributed in Tropical America from Panama to Brasil[1]. As a continuing study on the constituents of the pharmacologically interesting genus *Trattinickia* [2-6], we report in this paper the phytochemical study of the resin of *Trattinickia rhoifolia* Willd., "caraña". This material is used in the Venezuelan Folk Medicine in the Andes region, for the treatment of throat affections, teeth ache and, thorns and splinters removal from skin.

Experimental

General

Mps uncorrected; OR: ($CHCl_3$); IR (film); ^1H and ^{13}C NMR ($CDCl_3$) 400 and 100 MHz, respectively; with TMS as internal standard; HREIMS: direct inlet (70 eV); and HRFAB: Xe (10 KV) using 2-nitrobenzyl alcohol as matrix. GC/MS: SPB-1 column; t_i 60 ºC x 5 min; t_g 1 ºC/min; t_f 250 ºC x 10 min; Wiley 275 MS data base.

Plant material

Resin from *Trattinickia rhoifolia* Willd. (Burseraceae) was collected from Mucujepe, Mérida State, Venezuela, in March 1995. The plant material was characterized by comparison with voucher specimens already deposited at the herbarium of Facultad de Ciencias Forestales, Universidad de los Andes, Mérida, Venezuela (MER Nava 1-2, collected on March 1987).

Extraction, isolation and characterization

The crude resin of *T. rhoifolia* (193 g) was dissolved in 300 ml of methylene chloride and then diluted with *n*-hexane (5.7 L) to selectively precipitate the insoluble material. The major soluble fraction (174 g), dissolved in diethyl ether, was extracted with 5% aqueous $NaHCO_3$.

The neutral part was subjected to CC on silica gel with *n*-hexane/EtOAc gradient. Repeated CC of the 9:1 fraction using a gradient of *n*-hexane/methylene chloride yielded: *α*-selinene (23 mg), a mixture (7:1:2) of *α*-copaene, *α*-cubebene and *α*-ylangene (125 mg), *β*-selinene (3.9 g), atractylon (16 mg), asterolide (63 mg), biatractylolide (152 mg), **3** (43 mg), **2** (52 mg), a mixture (2:1) of *α*- and *β*-amyrins (21.3 g), atractylenolide III (132 mg), maniladiol (120 mg), and **1** (23 mg). Hydrocarbons mixture composition was analyzed by GC/MS. PTLC on silica gel plates of the mixture of amyrins (80 mg) with *n*-hexane-benzene (3:1) and eight developments yielded: *α*-amiryn (20 mg, Rf 0.71) and *β*-amiryn (10 mg, Rf 0.54).

The acid fraction (1.2 g) was methylated with an excess of diazomethane in Et_2O. Chromatography on silica gel-$AgNO_3$ (5%) using a *n*-hexane/Et_2O gradient yielded methyl (11ξ*H*)-eudesm-3-en-12-oate (7 mg), (11ξ*H*)-dihydro-*β*-costic acid (50 mg), *β*-costic acid (20 mg), and a mixture of methyl (11ξ)-8-oxoeudesm-4(15)-en-12-oates (100 mg). PTLC on silica gel of the mixture of 8-oxo-eudesmane derivatives, using benzene as eluyent and ten developments, yielded 11(*S*), **4** (41 mg, Rf 0.74) and 11(*R*), **5** (40 mg, Rf 0.58).

8β,9α-Dihydroxyeudesma-4(15),7(11)-dien-12,8-olide (**1**)

Colourless oil, $[\alpha]^{20}_D$ +10º (*c* 0.46, $CHCl_3$); IR (film) υ_{max} 3401, 3071, 2929, 2869, 1747, 1694, 1651, 1180, 1132, 1075, 1032, 886, 735 cm^{-1}. ^1H NMR, see Table 1. ^{13}C NMR, see Table 2. HMBC correlations: H_{1ax}/C-14; H_{1eq}/C-9; H_{2eq}/C-4; H_{3ax}/C-4, C-15; H_{6ax}/C-5, C-7, C-11; H_{6eq}/C-5, C-7, C-8, C-10, C-11; H_{9eq}/C-5, C-7, C-8, C-10, C-14; H_{13}/C-7, C-8, C-11, C-12; H_{14}/C-1, C-5, C-9, C-10; H_{15a}/C-4, C-5; H_{15b}/C-4, C-5. Significant NOESY correlations: H_{1ax}/H_{3ax}; H_{1ax}/H_{5ax}; H_{1eq}/H_{9eq}; H_{1eq}/H_{14}; H_{3ax}/H_{5ax}; H_{6ax}/H_{13}; H_{6ax}/H_{15a}; H_{6eq}/H_{13}; H_{6eq}/H_{15a}; H_{9eq}/H_{14}; H_{13}/H_{15a}; H_{13}/H_{15b}; H_{14}/H_{15a}; H_{14}/H_{15b}. EIMS *m/z* $[M]^{+\cdot}$ 264 (31), $[M - H_2O]^{+\cdot}$ 246 (39), 205 (39), 149 (62), $[C_3H_3O]^+$ 55 (100). HREIMS: found 264.1358; calc. for $C_{15}H_{20}O_4$ 264.1362.

Acetylation of **1**

An aliquot (10 mg) of **1** was dissolved in pyridine (0.5 ml) and 0.5 ml of acetic anhydride was added. The mixture was stirred at room temperature for 4 h, poured on ice, and extracted with Et_2O, and the ethereal layer washed with 2*N* HCl, $NaHCO_3$ (4%), and water, dried over $MgSO_4$, and evaporated under a vacuum to afford the diacetylated derivative **1a** (7 mg): colourless oil, $[\alpha]^{20}_D$ +14º (*c* 0.06, $CHCl_3$). IR (film) υ_{max} 2925, 2854, 1779, 1755, 1699, 1650, 1371, 1227, 1205, 1074, 1035, 994 cm^{-1}. ^1H NMR, see Table 1. ^{13}C NMR, see Table 2. Significant NOE differential correlations: H-14/H-1eq, H-2ax, H-6ax, H-9eq, H-15a, (C-8)-OCOC$\underline{H}_3$. EIMS *m/z* $[M]^{+\cdot}$ 348 (8), $[M - C_2H_2O]^{+\cdot}$ 306 (40), $[M - 2.C_2H_2O]^{+\cdot}$ 264 (29), 71 (55), $[C_3H_5O]^+$ 57 (100), $[C_3H_3O]^+$ 55 (86).

8β,9β-epoxyeudesma-4(15),7(11)-dien-12,8-olide (**2**)

Oil, $[\alpha]^{20}_D$ 164,5 º (c: 0,012). IR (*KBr*) υ_{max}: 3080, 2930, 2869, 1764, 1674, 1645, 1442, 1383, 1334, 1269, 1239, 1200, 1150, 1105, 1045, 1013, 988, 929, 893, 736 cm^{-1}. ^1H NMR, see table 1. ^{13}C NMR, see table 2. HMBC correlations (for each sub-unity): C-1/H_{9ax}, H_{14}; C-3/ H_{1ax}, H_{1eq}, H_{5ax}, H_{15a}, H_{15b}; C-4/H_{6ax}, H_{6eq}; C-5/H_{9ax}, H_{14}; C-7/H_{13}; C-8/H_{6ax}; C-9/H_{5ax}, H_{14}; C-10/H_{2ax}, H_{2eq}, H_{6ax}, H_{6eq}; C-11/H_{6ax}; C-12/H_{13}; C-14/H_{1eq}, H_{5ax}, H_{9ax}; C-15/H_{5ax}. EM (*m/z*): $[M]^{+\cdot}$ 246 (20), $[M - O]^+$ 230 (97), $[M - O - CH_3]^{+\cdot}$ 215 (65), $[C_7H_7]^{+\cdot}$ 91 (100), $[C_3H_3O]^+$ 55 (49). HREIMS: found 246.1253; calc. for $C_{15}H_{18^o}O_3$ 246.1256.

8,8'-bis [Eudesma-4(15),7(11)-dien-12,8β-olide] (**3**)

Colourless prisms, mp 200-202 ºC. $[\alpha]^{20}_D$ +204.2º (*c* 0.022, $CHCl_3$). IR (film) υ_{max} 3497, 3079, 2931, 2868, 2849, 1759, 1674, 1649, 1442, 1385, 1269, 1105, 1042, 1011, 889, 737 cm^{-1}. ^1H NMR, see Table 1. ^{13}C NMR, see Table 2. HMBC correlations: H_{1ax}/C-2, C-3, C-5, C-9, C-14; H_{1eq}/C-2, C-3, C-5, C-14; H_{2ax}/C-10; H_{2eq}/C-4, C-10; H_{3ax}/C-1, C-2, C-4, C-15; H_{3eq}/C-1, C-4, C-5, C-15; H_{5ax}/C-3, C-4, C-6, C-9, C-14, C-15; H_{6ax}/C-4, C-5, C-7, C-8, C-11; H_{6eq}/C-5, C-7, C-10, C-11; H_{9ax}/C-1, C-5, C-7, C-8, C-10, C-14; H_{9eq}/C-1, C-5, C-7, C-8, C-10, C-14; H_{13}/C-6, C-7, C-8, C-11, C-12; H_{14}/C-1, C-10; H_{15a}/C-4, C-5; H_{15b}/C-4, C-5. Significant NOESY correlations: H_{1ax}/H_{3ax}; H_{1ax}/H_{5ax}; H_{1eq}/H_{9eq}; H_{1eq}/H_{14}; H_{3ax}/H_{5ax}; H_{6ax}/H_{13}; H_{6ax}/H_{15a}; H_{6eq}/H_{13}; H_{6eq}/H_{15a}; H_{9eq}/H_{14}; H_{13}/H_{15a}; H_{13}/H_{15b}; H_{14}/H_{15a}; H_{14}/H_{15b}. EIMS *m/z* $[M]^{+\cdot}$ 462 (4), $[M/2]^+$ 231 (11), $[M/2 - CH_3]^{+\cdot}$ 216 (4), 77 (45), $[C_4H_5O]^+$ 69 (100), $[C_3H_5O]^+$ 57 (40). HREIMS: found 462.2761; calc. for $C_{30}H_{38}O_4$ 264.1362.

Reduction-lactonization of **5**

Compound **5** (18 mg) was subjected to reduction with $NaBH_4$ (4 mg) in MeOH (3 ml) at room temperature for 4 h. The solvent was evaporated under vacuum and the reaction mixture redissolved in methylene chloride (20 ml), washed with water to pH 7, dried over $MgSO_4$, evaporated, and purified by preparative TLC on silica gel 60 F_{254} plates, eluting with benzene (triple development) to give 11α,13-dihydroisoalantolactone (15 mg, Rf 0.41).

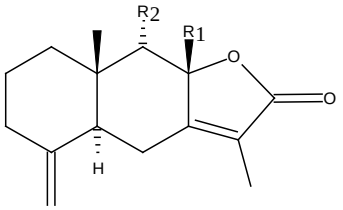
Molecular modeling

Calculations were performed on a Silicon Graphics Indigo computer. Structures of compounds were built using Macromodel version 4. Conformational analysis of each compound was performed by a Monte Carlo random search. All freely rotating bonds were searched with MM2 minimization[7].

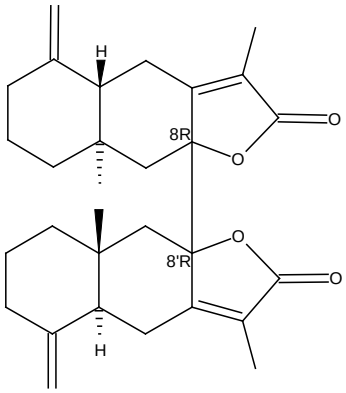
Results and discussion

The resin was dissolved in methylene chloride, degreased, and partitioned in acidic- and neutral portions. Repeated column chromatography and preparative TLC of the neutral part yielded the novel compounds **1**-**3** and the known compounds: *α*-selinene, *β*-selinene, atractylon, asterolide, biatractylolide**,** *α*-amyrin, *β*-amyrin, atractylenolide III**,** maniladiol, and eudesma-7(11), 8-dien-12,8-olide which were characterized by comparison with literature data[8-11]. Additionally, *α*-copaene, *α*-cubebene, and *α*-ylangene were characterized by GC/MS analysis and comparison with KI and MS data bases entries. The acidic portion was methylated with diazomethane and subsequently chromatographed to yield the known compounds: (11*ξH*)-eudesm-3-en-12-oic acid, (11*ξH*)-dihydro-*β*-costic acid, *β*-costic acid, (11*S*)-8-oxoeudesma-4(15),7(11)-dien-12-oic acid, **4**, and (11*R*)-8-oxoeudesma-4(15),7(11)-dien-12-oic acid, **5**, as methyl esters[8].

The molecular formula of compound **1** was assigned as $C_{15}H_{20}O_4$ by HREIMS (M^+ *m/z* 264.1358) and ^{13}C NMR spectral data. IR spectrum showed typical alcohol (3401 cm^{-1}), α,β-unsatured γ-lactone group (1747, 1180, and 1132 cm^{-1}), and exocyclic methylene (3071, 1651, and 886 cm^{-1}) absorptions. The ^1H NMR spectrum (Table 1) exhibited signals for two methyl groups [δ 1.03 (H-14) and δ 1.80 (H-13)], an oxygenated methine proton [δ 3.67, s, H-9eq], two olefinic methylene protons: [δ 4.57 (1H), s, H-15a] and [δ 4.84 (1H), s, H-15b], in addition to the other skeletal protons. The ^{13}C NMR spectra of **1** (Table 2), showed signals for an α,β-unsatured γ-lactone grouping [δ 173.1 (C-12), δ 158.9 (C-7), δ 123.9 (C-11) and δ 104.9 (C-8)], one exocyclic vinylidene group [δ 149.1 (C-4) and δ 107.0 (C-15)], one quaternary sp^3 hybridized carbon [δ 40.6 (C-10)], one tertiary oxygenated carbon [δ 78.5 (C-9)], one tertiary carbon [δ 44.3 (C-5)], four secondary carbons [δ 36.1 (C-3), δ 34.6 (C-1), δ 24.5 (C-6), and δ 22.1 (C-2)], and two methyl groups [δ 16.1 (C-14), and δ 8.3 (C-13)]. Its ^1H-^1H COSY NMR spectrum showed the expected proton correlations and the HMQC spectrum led us to the assignment of the ^1H-^{13}C correspondences. $J_{6ax,5ax}$ and $J_{6eq,5ax}$ values (12.5 and 3.3 Hz, respectively) supported the unequivocal assignment of the 5α-H configuration, and the strong NOE connectivities observed between H-1eq and H-9, and H-14 and H-9 led to establish the 9βH configuration. In order to determine the C-8 configuration, compound **1** was treated with acetic anhydride in pyridine to yield the diacetate **1a**. The NOE effects observed between the angular methyl group (δ 0.91, H-14), the proton H-9 (δ 5.40) and the acetate methyl group on C-8 (δ 2.10), showed that the three groups lie on the same side of the molecular plane, and therefore, the hemiacetallic acetate group (and hence, the 8-hydroxyl group) in compound **1** should be β oriented, and therefore, compound **1** was assigned as 8*β*,9*α*-dihydroxyeudesma-4(15),7(11)-dien-12,8-olide.



R_1	R_2	
β-OH	α-OH	**1**
β-OAc	α-OAc	**1a**
	β-epoxy	**2**



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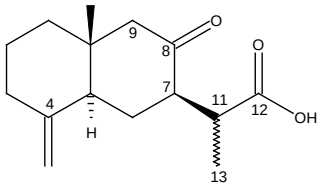

11S	**4**
11R	**5**

Compound **2** was obtained as colourless oil. The molecular formula $C_{15}H_{18}O_3$ was deduced from HREIMS data (M^+ *m/z* 246.1253). Its IR spectrum showed absorptions for α,β-unsatured γ-lactone (1764, 1150, and 1105 cm^{-1}) and exocyclic methylene (3080, 1645, and 893 cm^{-1}) functionalities, and its HREIMS showed a signal for *m/z* [M^+- 16] corresponding to the [O] loss, which its typical for oxyrane ring. The ^{13}C NMR spectrum was very similar to compound **1**, except for C-8 and C-9, which resounded at δ 88.3 and δ 39.2, respectively; these arguments, together with HMQC and HMBC correlations, put the epoxy moiety on C-8 and C-9 position. The epoxy orientation was determined by the NOE's correlations observed between H-9 (axial) and H-5ax, and H-1ax. In this disposition, the angular methyl group is strongly shielded (δ 0.64) by the exocyclic methylene π electron and the oxyranic oxygen. In conclusion, compound **2** should be 8β, 9β-epoxyeudesma-4(15),7(11)-dien-12,8-olide.

Compound **3** was obtained as a colourless crystalline solid from hexane-methylene chloride. Its IR spectrum showed absorptions for α,β-unsatured γ-lactone (1763, 1150, and 1108 cm^{-1}) and exocyclic methylene (3083, 1649, and 893 cm^{-1}) functionalities, and its HRMS showed a signal for M^+ at *m/z* 462.2750, corresponding to the molecular formula $C_{30}H_{38}O_4$. The ^{13}C NMR spectrum, however, showed only fifteen signals. These arguments, together with the fragmentation pattern of the mass spectrum (displaying no peaks in the M^+ - $M^+/2$ interval), suggested that the structure should correspond to that of a symmetrical dimeric sesquiterpenoid. The ^1H NMR spectrum (see Table 1) showed a very shielded singlet, assigned to the angular methyl groups [δ 0.47 (H-14 and H-14')], another singlet corresponding to the methyl groups attached to the olefins [δ 1.75 (H-13 and H-13')], two doublets signals coupled between its corresponding to 9 and 9' position methylene protons [δ 1.98, (H-9ax and H-9'ax) and δ 2.28, (H-9eq and H-9'eq)], two olefinic methylene proton signals [δ 4.60 and δ 4.83], and the other signals corresponding to the skeleton rest. Proton-proton connectivities were established by the ^1H - ^1H COSY NMR spectrum. The ^{13}C NMR spectra of **3** (see Table 2) exhibited signals for one carbonyl [δ 172.6 (C-12), α,β-unsatured γ-lactone], three non-protonated olefinic carbons [δ 163.3 (C-7), δ 148.8 (C-4), and δ 125.4 (C-11)], one olefinic methylene [δ 107.1 (C-15)], two sp^3 non-protonated carbons [δ 89.3 (C-8) and δ 36.5 (C-10)], five methylenes [δ 47.0 (C-9), δ 42.1 (C-1), δ 36.8 (C-3), δ 24.8 (C-6), and δ 22.7 (C-2)], and two methyl groups [δ 19.0 (C-14) and δ 8.6 (C-13)]. Newly, the combined analysis of HMQC and HMBC spectra (see Experimental Section), led the identification of the eudesmane skeleton for each monomeric moiety of compound **3**. The chemical shift and multiplicity (quaternary) of the lactone ring carbon (δ 89.3) suggested that the union of the two sesquiterpenic moieties occurred between C-8 and C-8'. The coupling constant values found for the signals at δ 2.62 and δ 2.79 allowed that the configurations to be established at C-5 (C-5'), while the spatial arrangement of significant hydrogen atoms was established by NOESY correlations for **3**. The 8*R*,8'*R* configuration was postulated for **3** considering that molecular modeling calculations showed that in the 8*R*,8'*R* configuration, both sp^3 hybridized oxygen atoms were preferably located in the *anti* disposition (see, figure 1), and the high shielding displayed by the signal assigned to the angular methyl group, δ 0.47, compared to δ 1.13 in biatractylolide, 8*S*,8'*S* configuration (Lin et al., 1997), occurs because B and B' rings were in the boat conformation, with H-14 and H-14' protons lying into the shielding zone of the two olefinic moieties $\Delta^{4(15)}$, $\Delta^{7(11)}$ and $\Delta^{4'(15')}$, $\Delta^{7'(11')}$, respectively. Biatractylolide, was also isolated by our group from this plant[6]. In conclusion, the structure of the 8,8' dimer of 8-*epi*-asterolide is proposed for compound **3**, suggesting for it the name of biepiatractylolide.

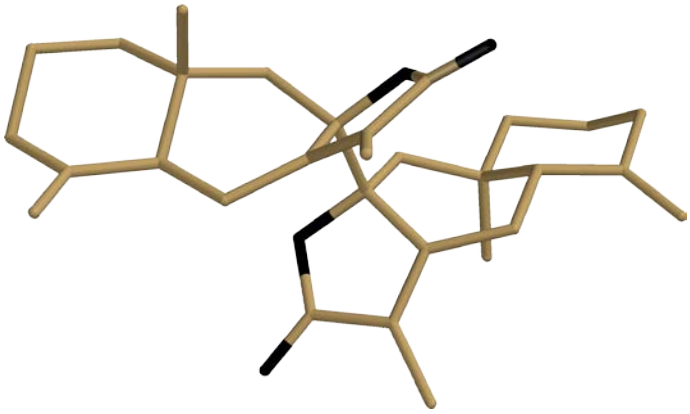

Figure 1: Three-dimensional structure of the lowest energy conformer of compound **3** obtained by molecular modeling.

Compounds **4** and **5** were described by Bohlmann and coworkers as semi-synthetic derivatives of isoasterolides A and B[8]. Due the respective configuration at C-11 remained unassigned, and spectral data reported were not complete and some of them erroneous, we reported the NMR data and discussed the structural assignation for both substances.

Molecular modeling studies performed for **4** and **5** enabled in both epimers H-7ax and H-11 to be placed in an *anti* disposition to one another, and the C-11 – H-11 bonds and methyl ester groups being coplanar, and the carbonyl-oxygen atoms to be in *anti* disposition relative to H-11. In the 11*S* epimer, H-6ax lies in a shielding zone of the ester carbonyl; on the other hand, H-6eq lies in the deshielding region originated by the lone pair electrons of the ester sp^3 oxygen atom. Accordingly, the chemical shift expected for H-6ax should be downfield in the 11*R* compound with respect to the 11*S* epimer. In contrast, the chemical shift expected for H-6eq should be found upfield in the 11*R* epimer relative to the 11*S* epimer. Accordingly, compound **4** ($\delta_{H\text{-}6ax}$ 1.52 and $\delta_{H\text{-}6eq}$ 2.04) should be the 11*S* epimer, and 11*R* stereochemistry may be assigned to compound **5** ($\delta_{H\text{-}6ax}$ 1.79 and $\delta_{H\text{-}6eq}$ 1.94).

The unequivocal assignment of the configuration at C-11 for **4** and **5** was performed by reduction of the keto carbonyl group of **5** with $NaBH_4$ followed by *in situ* lactonization; the product generated was the (11*R*) 13-dihydroisoalantolactone[14]. Accordingly, compound **5** should have the same C-11 configuration (11*R*), and compound **4** should have the 11*S* configuration. Therefore, compounds **4** and **5** (compounds **19** and **18** in reference 8, respectively) were assigned as (11*S*)-8-oxoeudesm-4(15)-en-12-oic acid methyl ester and (11*R*)-8-oxoeudesm-4(15)-en-12-oic acid methyl ester, respectively.

Table 1: ^{1}H NMR assignments for compounds **1**, **1a**, **2**, **3**, **4** and **5**.

H_n	**Δ, multiplicity, *J*(Hz)**					
	1	**1a**[a]	**2**	**3**[b]	**4**[c]	**5**[d]
H-1_{ax}	1.99, td (13.0; 6.0)	1.93, td (13.2, 2.0)	1.26, td (14.0; 2.2)	1.39, td (12.4; 2.6)	1.50, td (12.6; 3.5)	1.49, ddt (12.7; 10.9; 4.0)
H-1_{eq}	1.28, ddd (13.0; 3.4; 2.2)	1.28, dt (13.2, 2.0)	1,57, m	1.53, dt (12.4; 2.6)	1.54, dt (12.6; 3.9)	1.49, ddt (10.9; 3.7; 2.3)
H-2_{ax}	1.52 – 1.70, m	1.62, m	1.51, m	1.44, qt (12.4; 2.6)	1.53, qt (12.6; 3.9)	1.55, qdd (12.7; 3.7; 2.3)
H-2_{eq}		1.68, m	1.72, m	1.60, m	1.66; dq (12.6; 3.9)	1.65, dddt (13.1; 12.7; 4.7; 2.3)
H-3_{ax}	1.91, td (11.6; 6.8)	1.89, td (13.1, 1.4)	1.98, td (14.2; 4.5)	2.05, td (12.4; 4.2)	2.08, tdd (12.6; 3.9; 1.2)	2.05, dddd (13.1; 12.7; 4.7; 1.5)
H-3_{eq}	2.31, dt (11.6; 1.7)	2.34, dt (13.1, 1.2)	2.40, d(br) (14.2)	2.33, dt (12.4; 2.6)	2.36, dtd (12.6; 3.9; 1.2)	2.36, dtd (13.1; 2.3; 1.5)
H-5_{ax}	2.28, dd (12.5; 3.3)	2.20, dd (13.2, 3.2)	2.80, dd (12.6; 5.1)	2.79, dd (10.6; 10.0)	2.37, ddt (13.0; 3.4; 1.2)	1.49, ddt (12.6; 6.1; 1.5)
H-6_{ax}	2.40, dd (13.1; 12.5)	2.32, td (13.2, 1.4)	2.68, dd (19.7; 12.6)	2.62, dd (17.5; 10.6)	1.52, q (13.0)	1.79, q (12.6)
H-6_{eq}	2.54, dd (13.1; 3.3)	2.71, dd (13.2, 3.2)	2.85, d (19.7; 5.1)	2.15, ddd (17.5; 10.0; 1.9)	2.04, ddd (13.0; 6.0; 3.4)	1. 94, ddd (12.6; 6.1; 3.5)
H-7_{ax}	-	-	-	-	2.82, dt (13.0; 6.0)	2.68, dt (12.6; 6.1)
H-9_{ax}	-	-	2.50, s	1.98, d (14.9)	2.17, d (13.0)	2.18, d (13.2)
H-9_{eq}	3.67, s	5.40, s	-	2.28, d (14.9)	2.33, d (13.0)	2.28, d (13.2)
H-11	-	-	-	-	2.77, qd (6.9; 6.0)	2.84, qd (7.1; 6.1)
H-13	1.80, s	1.92, d (1.4)	1.79, s	1.75, d (1.9)	1.16, d (6.9)	1.22, d (7.1)
H-14	1.03, s	0.91, s	0.64, s	0.47, s	0.66, s	0.71, s
H-15a	4.57, s	4.65, d (1.2)	4.74, s	4.60, s	4.50, q (1.2)	4.50, q (1.5)
H-15b	4.84, s	4.93, d (1.2)	4.94, s	4.83, s	4.83, q (1.2)	4.81, q (1.5)

a $\delta_{H(C8\text{-}OCO\underline{Me})}$: 2.10, s; $\delta_{H(C9\text{-}OCO\underline{Me})}$: 2.06, s

b $\delta_{H's}$ corresponds to H_n and $H_{n'}$

c $\delta_{H(C12\text{-}O\underline{Me})}$: 3.68, s

d $\delta_{H(C12\text{-}O\underline{Me})}$: 3.67, s

Table 2: ^{13}C NMR Spectral Data ($CDCl_3$, 100 MHz) for compounds **1**, **1a**, **2**, **3**, **4** and **5**.

C_n	δ_C					
	1	**1a**[a]	**2**	**3**[b]	**4**[c]	**5**[d]
C-1	34.6	34.1	35.6	42.1	41.3	41.4
C-2	22.1	21.6	22.5	22.7	22.9	23.0
C-3	36.1	35.6	36.6	36.8	36.5	36.6
C-4	149.1	147.7	147.7	148.1	148.5	148.5
C-5	44.3	45.4	48.8	42.6	48.3	48.5
C-6	24.5	24.2	25.4	24.8	28.3	28.9
C-7	158.9	154.8	160.1	163.3	52.1	52.6
C-8	104.9	102.2	88.3	89.3	209.9	209.3
C-9	78.5	76.1	39.2	47.0	55.7	56.0
C-10	40.6	40.0	38.4	36.5	40.6	40.6
C-11	123.9	125.4	123.2	125.4	38.5	38.6
C-12	173.1	171.2	172.8	172.6	176.7	175.7
C-13	8.3	8.4	8.7	8.6	14.1	14.5
C-14	16.1	15.4	19.6	19.0	17.0	17.1
C-15	107.0	107.6	108.5	107.1	107.1	107.2

[a] $\delta_{C8\text{-}O\underline{C}OMe}$: 169.2, $\delta_{C8\text{-}OCO\underline{Me}}$: 21.7, $\delta_{C9\text{-}O\underline{C}OMe}$: 167.4, $\delta_{C9\text{-}OCO\underline{Me}}$: 20.4 [b] $\delta_{C's}$ corresponds to C_n and $C_{n'}$
[c] $\delta_{C12\text{-}O\underline{Me}}$: 51.7 [d] $\delta_{C12\text{-}O\underline{Me}}$: 51.5

Conclusions

The existence of eudesmane sesquiterpenoids in resins from Neotropical Burseraceae species, apparently afford a chemotaxonomic support to the assignation of *Trattinickia* genus to tribe Protieae.

By other hand, the oxidized eudesmane occurrence into resin can be due to the oxidative process occurring in the resin during its aging process still in the tree trunks since the bark laceration to resin collection (near two months). This assertion should be considered because the fresh exudates are a clear viscous liquid whereas the resin is a brown pasty gum. It is important to stand out that none of the isolated products in this work is colored and in consequence its natural occurrence can be considered. At present, a comparative study of the fresh exudates and resins from this and other species of Burseraceae by GC/MS are being made by us.

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