

A New Sesquiterpene from *Trichilia casarettii* (Meliaceae)

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Abstract

The dichloromethane extract of the air-dried stems of *Trichilia casarettii* afforded a new sesquiterpene (1), lupeol, stigmasterol, campesterol and sitosterol. The structure of 1 was elucidated by extensive one- and two-dimensional nuclear magnetic resonance and mass spectrometry.

Keywords: *Trichilia Casarettii*, *Meliaceae*, *Sesquiterpene*

1. Introduction

The Meliaceae family has attracted much interest among bioproduction phytochemists because of its very complex and diverse chemical structures and its biological activity, mainly against insects [1-3]. The *Trichilia* genus (Meliaceae) includes about 230 species distributed throughout tropical America which are recognized for their significant economic importance and high commercial value. The genus is rich in terpenoids, including triterpenes, limonoids, steroids and other terpenes derivatives [3-5].

In previous the activity of aqueous extract of leaves and twigs from *T. casarettii* was evaluated on *Spodoptera frugiperda* (J. E. Smith) development in laboratory conditions [6]. To the best of our knowledge, the literature reports no chemical investigation evaluation of *T. casarettii* native of Americas [7]. This stimulated our interest in the present work, involving isolation and structural elucidation of the constituents of the stems of this species. Then, we report the isolation of new sesquiterpene **1** (Figure 1) of *T. casarettii* DC. The stems also afforded lupeol, stigmasterol, campesterol, sitosterol and fatty acid esters.

The stems from *T. casarettii* DC., was collected on November 2006, at Vale do Rio Doce Cia., Linhares City, Espírito Santo State, Brazil. A voucher specimen (N^o 449) was deposited at Vale do Rio Doce Cia. Herbarium.

2. Results and Discussion

Compound **1** (Figure 1) was obtained as white powder (MeOH), mp 121-122°C, and which is optically active with an $[\alpha]_D^{23} = -18.1^\circ$ (CHCl₃, *c* 0.002). Its IR spectrum (KBr disk) obtained in spectrometer Shimadzu, model FTIR-8300, showed bands at ν_{\max} 3433 (O-H stretching), 3394 (O-H stretching) cm⁻¹. Comparative analysis using spectrometer Brüker, DRX model [(operating at 400 (¹H) and 100 (¹³C) MHz, respectively, in pyridine-*d*₅)] of the {¹H}- and DEPT 135°-¹³C NMR spectra (Table 1) revealed signals corresponding to 15 carbon atoms. These data allowed us to recognize the presence of signals corresponding to three nonhydrogenated carbons [(C)₃: all sp³ (including two bound to an oxygen atoms at δ_C 71.51 and 71.58)], two methine [(CH)₂: all sp³, two α to a carbinolic carbon atom at δ_C 55.64/ δ_H 1.58 and δ_C 51.14/ δ_H 1.60, correlated in the HMQC spectrum with ¹H chemical

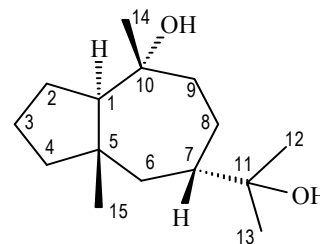


Figure 1. Chemical structure of ambrosanoli-10, 11-diol (1).

Table 1. ^{13}C (100 MHz) and ^1H NMR (400 MHz) data of compound **1** in pyridine-*d*₅, δ in ppm, J in Hz and multiplicities, in parenthesis.*

| | | HMQC | | HMBC | |
|-----------------------|---------------------|------------------------------------|-------------------|-------------------|--------------------|
| C | δ_{C} | δ_{H} | $^2J_{\text{CH}}$ | $^3J_{\text{CH}}$ | |
| 5 | 35.08 | - | 2H-4; 3H-15 | | H-7 |
| 10 | 71.51 | - | 2H-9; 3H-14 | | |
| 11 | 71.58 | - | H-7; 3H-12; 3H-13 | | |
| CH | | | | | |
| 1 | 55.64 | 1.60-1.52 (m) | | | 2H-9; 3H-14; 3H-15 |
| 7 | 51.14 | 1.62-1.54 (m) | | | 3H-12; 3H-13 |
| CH₂ | | | | | |
| 2 | 21.01 | 1.60-1.56 (m) 1.54-1.50 (m) | | | |
| 3 | 23.47 | 1.85 (br s, 11.0) 1.60-1.57 (m) | 2H-2; 2H-4 | | |
| 4 | 45.77 | 1.44-1.40 (m) 1.14-1.12 (m) | 2H-3 | | 3H-15 |
| 6 | 42.08 | 1.38-1.36 (m) 1.10-1.02 (m) | | | 2H-4; 3H-15 |
| 8 | 22.58 | 2.64 (br s, 12.0) 1.39-1.37 (m) | | | |
| 9 | 44.55 | 1.98 (br s, 12.0) 1.75-1.78 (m) | | | 3H-14 |
| CH₃ | | | | | |
| 12 | 28.24 | 1.38 (s) | | | H-7; 3H-13 |
| 13 | 28.20 | 1.38 (s) | | | H-7; 3H-12 |
| 14 | 23.51 | 1.31 (s) | | | 2H-9 |
| 15 | 19.56 | 0.93 (s) | | | 2H-4; 2H-6 |

shifts, respectively], six methylene [(CH₂)₆, including one α to a carbinolic carbon atom at δ_{C} 44.55/ δ_{H} 1.98 and 1.72] and four methyl [(CH₃)₄: including three linked to a carbinolic carbon atom at δ_{C} 28.24/ δ_{H} 1.38, δ_{C} 28.20/ δ_{H} 1.38 and δ_{C} 23.51/ δ_{H} 1.31] carbon atoms, allowing us to deduce the expanded molecular formulae (C)(C-OH)₂(CH)₂(CH₂)₆(CH₃)₄ = C₁₅H₂₈O₂ for **1**. The high-resolution electrospray ionization mass spectra (HR-ESIMS) of **1** obtained in mass spectrometer, model LCMS-IT-TOF (225-07100-34, Shimadzu) showed a pseudomolecular ion at m/z 263.1988 [M+Na]⁺, with the calculated value for C₁₅H₂₈O₂Na being 263.1987. The molecular formula indicated an index of hydrogen deficiency of two. Thus, with ^1H and ^{13}C NMR spectral data and the compound bicyclic is compatible with the carbon skeleton sesquiterpenic of the ambrosanolide type [8].

In the ^1H NMR spectrum, three singlet signals were observed at δ_{H} 1.38 and δ_{H} 1.31, characteristic of a methyl groups linked to two carbinolic carbons, and one singlet signal at δ_{H} 0.93, corresponding to the signals at δ_{C} 28.24 (CH₃-12), 28.20 (CH₃-13), 23.51 (CH₃-14) and 19.56 (CH₃-15) in the ^{13}C NMR spectrum, suggesting the presence of two hydroxyl groups. The HMBC spectrum allowed us to confirm these long-range correlations (**Table 1**) through the signals corresponding to C-10 (δ_{C}

71.51) with the singlet observed at δ_{H} 1.31 (3H-14, $^2J_{\text{CH}}$) and C-11 (δ_{C} 71.58) with the two singlets observed at δ_{H} 1.38 (3H-12 and 3H-13, $^2J_{\text{CH}}$). This deduction was corroborated by the long-range correlations of methyne carbons CH-1 (δ_{C} 55.64) with both 3H-14 and 3H-15 (δ_{H} 1.31 and 0.93, $^3J_{\text{CH}}$) and CH-7 (δ_{C} 51.14) with both 3H-12 and 3H-13 (δ_{H} 1.38, $^3J_{\text{CH}}$) observed in the HMBC spectrum (**Table 1**). Thus, these data allowed us to recognize the presence of hydroxyl groups at C-10 (δ_{C} 71.51) and C-11 (δ_{C} 71.58).

The relative stereochemistry of **1** was determined from the spatial dipolar interaction revealed by the ^1H - ^1H -NOESY spectrum, summarized in **Figure 2**. The ^1H - ^1H -NOESY spectrum of **1** allowed characterization of the ring-junction (CH-1 with C-5) of the bicyclic system involving the seven and five-rings as *trans*. The relative stereochemistry indicated in **1** was deduced by the spatial dipolar interaction observed in the ^1H - ^1H -NOESY spectrum between hydrogen atom H-7 with H₃-14 and H₃-15 indicating that both are β -oriented. The spatial dipolar interaction observed between H-1 and H-6b and absence of spatial interaction between H-1 with both, H₃-14 and H₃-15, respectively, indicating that H-1 was α -oriented in agreement with a *trans* ring-junction.

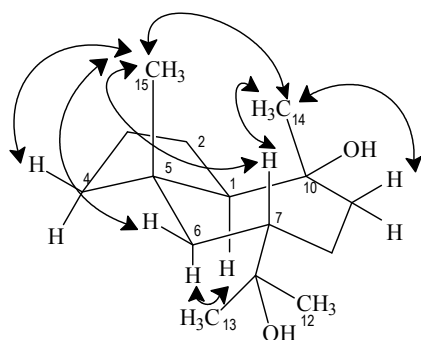


Figure 2. Selected NOESY correlations and relative stereochemistry for compound **1**. Arrows denote the main NOESY correlations.

Additional spatial interaction is shown in **Figure 2**. Therefore, the structure of the new sesquiterpene (**Figure 1**) isolated from *T. casarettii* was defined as ambrosanoli-10,11-diol (**1**) (30 mg, 0.0433%).

The structures of lupeol [9], β -sitosterol [10] and stigmasterol [10] were deduced by comparison of their ^1H and ^{13}C NMR spectral data with those reported in the literature.

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