



Vibrational spectra and DFT calculations of sonderianin diterpene

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ABSTRACT

In the present study, the natural product sonderianin diterpene ($C_{21}H_{26}O_4$), a diterpenoid isolated from *Croton blanchetianus*, with potential application in the drug industry, was characterized by nuclear magnetic resonance, infrared and Raman spectroscopy. Vibrational spectra were supported by Density Functional Theory calculations. Infrared and Raman spectra of sonderianin were recorded at ambient temperature in the regions from 400 cm^{-1} to 3600 cm^{-1} and from 40 cm^{-1} to 3500 cm^{-1} , respectively. DFT calculations with the hybrid functional B3LYP and the basis set 6–31 G(d,p) were performed with the purpose of obtaining information on the structural and vibrational properties of this organic compound. A comparison with experimental spectra allowed us to assign all of the normal modes of the crystal. The assignment of the normal modes was carried out by means of potential energy distribution.

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1. Introduction

Euphorbiaceae family stands as one of the largest among the dicotyledones, comprising about 300 genera and 7500 species. In Brazil, there are 72 genera and about 1300 species in all vegetation types, being the genus *Croton* the second most important, with about 700 species [1]. Several of these species find application in the treatment of a variety of diseases, and some of the isolated compounds are promising candidates in drug development. One of these species is *Croton blanchetianus*, formerly named *Croton sonderianus*, and popularly known as “marmeleiro preto”, which is restricted to the Brazilian semi-arid region. This plant is used in folk medicine to treat stomachache, uterine bleeding, and inflamed hemorrhoids [2]. The ethno-pharmacological information refers to this plant as having antibacterial and antifungal properties [3–7], antinociceptive activity [8], and activity against *Aedes aegypti* mosquito [9]. Also, the extract from *C. blanchetianus* has been considered as an alternative means to control dental pathogens [10]

and might be useful as a new source of therapeutic agents for the treatment of asthma [11].

As it should be expected, these plants present a rich set of substances. Among them, one can find sonderianin diterpene, with molecular formula $C_{21}H_{26}O_4$. This compound was firstly isolated from the stems of *C. blanchetianus* and its structure was elucidated by Nuclear Magnetic Resonance (NMR) and by X-ray crystallography analysis [4]. Other studies show that it can also be isolated from *Croton urucurana* [12–14].

Vibrational spectroscopy study of active substances extracted from medicinal plants is essential to provide detailed information about their structural and vibrational properties [15–20]. Up to now, neither experimental nor computational study on the vibrational properties of the sonderianin diterpene has been published in the literature. Therefore, the present investigation was undertaken to fill this gap and present the vibrational spectra of this molecule, with assignment of the various normal modes. In this study we report the characterization of sonderianin diterpene crystal, which was isolated from the stems of *C. blanchetianus*, by means of nuclear magnetic resonance (NMR), Fourier transform Raman (FT-Raman) and Fourier transform infrared (FT-IR) spectroscopy, as well as Density Functional Theory (DFT) calculations. A

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comparison with experimental spectra allowed us to assign all of the normal modes of the crystal. A complete description of the normal modes was carried out by considering the Potential Energy Distribution (PED).

2. Materials and methods

2.1. Sample preparation

Stems from *C. blanchetianus* were collected in March, 2011, in Sobral, Ceará State, Brazil. The sample material was identified by Dr. D.S. Carneiro-Torres at Herbario Francisco José de Abreu Mattos, Biology Department, in the State University Vale do Acaraú, Sobral, Ceará State, Brazil, where an exsiccate was deposited under registry number 14986.

2.2. Extraction and isolation

C. blanchetianus stem bark was dried at room temperature, followed by grinding and cold extraction with methanol for 3 days. The resulting solution was distilled under reduced pressure to give the methanol extract (89.33 g). The extract was adsorbed on silica gel and subjected to chromatography column using the following eluents: *n*-hexane, chloroform, ethyl acetate and methanol. The *n*-hexane extract (21.51 g) was reintroduced in the column and eluted with: *n*-hexane (F 1–10), *n*-hexane/ethyl acetate (9:1 F 11–20), *n*-hexane/ethyl acetate (8:2 F 21–30), *n*-hexane/ethyl acetate (7:3 F 31–40), *n*-hexane/ethyl acetate (6:4 F 41–50), *n*-hexane/ethyl acetate (1:1 F 51–60), *n*-hexane/ethyl acetate (4:6 F 61–70), *n*-hexane/ethyl acetate (3:7 F 71–80), *n*-hexane/ethyl acetate (2:8 F 91–100), ethyl acetate (F 100–110). Fractions 23–28 yielded a white crystalline solid identified as the sonderianin diterpene.

Column adsorption chromatography was carried out with silica gel 60 (63–200 μm , 70–230 mesh, Vetec). Column length and diameter were varied according to sample amount. Thin Layer Chromatography (TLC) used aluminum chromatoplates TLC 20 \times 20 cm with silica gel 60 GF₂₅₄ (Merck). Substances on the plates were revealed by exposing to a vanillin solution followed by heating.

2.3. NMR measurements

1D and 2D NMR experiments were performed on a Bruker Avance DRX-500 spectrometer (¹H 500 MHz, ¹³C 125 MHz) equipped with a 5 mm inverse detection z-gradient probe. ¹H and ¹³C NMR spectra were measured at 27 °C using CDCl₃ as the solvent (0.6 mL); chemical shifts were given in ppm (δ_{C} and δ_{H}), relative to residual CDCl₃ (7.24 and 77.0 ppm).

2.4. Raman and IR measurements

Raman spectrum was obtained using a Bruker RFS100/S FTR system and a D418-T detector, with a Nd:YAG laser emitting at 1064 nm as the excitation source. Infrared spectrum was obtained using a Cary 660 FT-IR spectrometer.

FT-Raman spectrum was collected at room temperature from samples confined in screw cap standard chromatographic glass vials, at a nominal resolution of 4 cm⁻¹, accumulating 60 scans per spectrum and using a laser out put power of 150 mW, in the spectral range from 40 to 4000 cm⁻¹. FT-IR spectrum was recorded at room temperature from sample in a KBr pellet in the wave-number range from 400 to 4000 cm⁻¹; with a resolution of 4 cm⁻¹ and accumulating 32 scans per spectrum.

2.5. Computational method

Calculations using Density Functional Theory (DFT) were carried out using the *Gaussian09* package [21]. The B3LYP functional was used with the 6-31G(d,p) basis set. The molecular structure of sonderianin in the DFT calculations corresponds to a single molecule of the unit cell described in Ref. [4], taken from the Cambridge Structural Database [22]. The calculations started with geometry optimization, and then the wavenumbers and the atomic displacements for each vibrational mode were calculated. No negative wavenumbers were obtained, indicating that a true minimum of the potential energy surface was found in the optimization. The calculated vibrational wavenumbers were adjusted by a scale factor in order to compare with experimental Raman and IR data. This is done in order to minimize the overall deviation. Following the procedure described by Wong [23] and Scott and Radom [24], the scale factor was calculated by fitting the theoretical wavenumber values to the experimental ones (from FT-Raman spectrum). After successive adjustments, the value of the scale factor was found to be 0.9512, with an overall root mean square error of 20.1 cm⁻¹. The description of the normal modes of vibration was analyzed in terms of the Potential Energy Distribution (PED) contributions using GAR2PED program [25]. The normal mode analysis was performed and the PED was calculated along the internal coordinates using localized symmetry [26,27]. For this purpose, a complete set of 147 internal coordinates were defined using Pulay's recommendations [26]. Visualization and confirmation of calculated data were carried out by using the Chemcraft program [28].

3. Results and discussions

Sonderianin diterpene, extracted from *C. blanchetianus*, is a white crystalline solid, which was shown to be pure by TLC analysis. NMR spectral data, shown in Table 1, is in good agreement with the experimental values presented in Ref. [4]. Its structure is shown in

Table 1
Comparative NMR spectral data of sonderianin.

	Sonderianin [this work]		Sonderianin [from Ref. [4]]	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
C				
4	142.6	–	142.3	–
5	37.8	–	37.6	–
9	51.4	–	51.6	–
13	125.9	–	125.6	–
19	167.7	–	164.5	–
20	176.8	–	173.0	–
CH				
3	135.6	6.53 (t, 3.0)	135.3	6.53 (t, 3.0)
8	40.6	1.49 (m)	40.4	1.48 (m)
10	51.8	1.59 (dd, 10.0, 4.0)	52.4	1.59 (dd, 10.0, 4.0)
12	71.8	5.39 (t, 8.5)	71.6	5.40 (t, 8.5)
14	108.3	6.39 (m)	108.0	6.40 (m)
15	144.2	7.44 (m)	143.8	7.45 (m)
16	139.6	7.42 (m)	139.5	7.43 (m)
CH₂				
1	19.9	3.49–2.20 1.90–1.70	19.7	3.49–2.20 1.90–1.70
2	26.9	2.49–2.20	26.8	2.49–2.20
6		2.40 1.90–1.70		2.40 1.90–1.70
7	26.7	2.08 (m) 1.18 (m)	26.5	2.06 (m) 1.18 (m)
11	44.9	2.39 (d, 8.5)	44.7	2.40 (d, 8.5)
CH₃				
17	16.9	1.01 (d, 7.0)	16.8	1.02 (d,b 7.0)
18	19.9	1.45 (s)	19.7	1.46 (s)
MeO	52.7	3.69 (s)	53.3	3.70 (s)

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