Cyrneine E, A New Cyathane Diterpene from *Sarcodon cyrneus*

Maria Carla Marcotullio*, Ornelio Rosati, Federica Maltese and Federica Messina

*Dipartimento di Chimica e Tecnologia del Farmaco, Università degli Studi di Perugia, Via del Liceo, 1, 06123 Perugia, Italy*

(Received September 10, 2012; Revised March 5, 2013; Accepted May 6, 2013)

**Abstract:** A new cyathane diterpene, cyrneine E (1) was isolated from the mushroom *Sarcodon cyrneus*. The structure of the novel compound was determined by analysis of its spectroscopic data.

**Keywords:** Cyrneine E; *Sarcodon cyrneus*; cyathane diterpenes.

1. **Plant Source**

Continuing our phytochemical studies on *S. cyrneus* (Bankeraceae), we isolated and identified a new cyathane diterpene named cyrneine E (1).

The mushroom was collected in October 2004 near Perugia (Italy) and identified by Prof. R. Pagiotti. A voucher specimen (RP#62) is deposited at the Dipartimento di Biologia Applicata-Sezione Biologia Vegetale e Geobotanica, Università degli Studi di Perugia.

2. **Previous Studies**

Cyathane diterpenes, cyrneines A and B [1], C and D [2] and glaucopine C [2, 3] were previously isolated from *S. cyrneus*. Cyrneines A and B resulted able to induce neurite outgrowth in a Rac1-dependent mechanism in PC12 cells [4], while cyrneine C and D failed to induce neurite outgrowth in PC12 cells, showing only a weak activity in inducing NGF expression in 1321N1 human astrocytoma cells [2].

3. **Present Study**

The lyophilized fruiting bodies of *S. cyrneus* (30 g) were extracted with MeOH (1 L) at room temperature for 24 h and then filtered. The filtrate was concentrated under vacuum to give 8.6 g of crude extract that was diluted with EtOAc and washed three times with H₂O. The organic phase was dried over Na₂SO₄, filtered and evaporated giving 1.84 g of a brown syrup (MII) that was subject to

* Corresponding author: E-mail: marcotu@unipg.it; mariacarla.marcotullio@unipg.it
Tel.: +39-075-585-5104; Fax: +39-075-585-5116

The article was published by Academy of Chemistry of Globe Publications

www.acgpubs.org/RNP © Published 5/28/2013 EISSN: 1307-6167
column chromatography (silica gel, CH₂Cl₂-EtOAc 10% → 100%) yielding 16 fractions. An amount (37 mg) of fraction MII-4 (54 mg) (eluted with CH₂Cl₂-EtOAc 9:1) was further purified (silica gel, CH₂Cl₂-EtOAc 19:1) to give 3 fractions (MII4 a-c). Fraction MII4-a was constituted by pure cyrneine E (1) (15 mg).

**Cyrneine E (1):** yellowish oil; [α]D25.4 - 78.2° (c 0.22, CH₂Cl₂); IR νmax (neat): = 2930, 1700, 1637, 1450 cm⁻¹; ¹H NMR (400 MHz, CD₃OD): δ (ppm) = 1.00 (3H, s, H-16), 1.15 (3H, s, H-17), 1.01 (3H, d, J = 6.9 Hz, H-19 or H-20), 1.03 (3H, d, J = 7.0 Hz, H-20 or H-19), 1.14-1.16 (2H, m, H-8), 2.00-2.10 (1H, m, H-7α), 2.90-3.05 (4H, m, H-2, H-10), 3.35 (1H, d, J = 13.9 Hz, H-13α), 3.45 (1H, dd, J = 2.0, 11.5 Hz, H-5), 6.82 (1H, m, H-11), 9.31 (1H, s, H-15); ¹³C NMR (100.62 MHz, CD₃OD): δ (ppm) = 12.1 (CH₃, C-17), 18.7 (CH₃, C-16), 20.5 (CH₃, C-19α), 20.9 (CH₃, C-20), 27.2 (CH, C-18), 29.0 (CH₂, C-7), 31.6 (CH₂, C-8), 31.8 (CH₂, C-10), 34.3 (CH₂, C-13), 40.3 (CH₂, C-2), 40.3 (CH, C-5), 54.3 (C, C-6), 54.9 (C, C-9), 135.5 (C, C-4), 137.1 (C, C-3), 135.8 (C, C-12), 153.7 (CH, C-11), 193.1 (CH, C-15), 211.2 (C, C-1), 221.7 (C, C-14); MS (rel. int.): m/z 314 [M⁺] (26), 299 (100), 271 (25), 243 (19); HREIMS: m/z 314.4164 (calcd. 314.4186 for C₂₀H₂₆O₃).

**Figure 1.** Key COSY and HMBC correlations in cyrneine E (1) isolated from *S. cyrneus.*

Compound 1, was isolated as yellowish oil. The MS of 1 revealed a molecular weight of 314.4164 consistent with the molecular formula C₂₀H₂₆O₃, which was confirmed by HREIMS analysis. The IR spectrum showed absorptions at 1700, 1637 cm⁻¹ implying two carbonyl functions confirmed by the signals at δ 221.7 and 211.2 ppm in a JMODXH (J-modulated spin-echo; C, H) spectrum. The carbon resonance at δ 193.1 (CH), 153.7 (CH) and 135.8 (C) ppm showed the presence of an α,β-unsaturated aldehyde. The olefinic signals at δ 137.1 and 135.5 indicated the presence of a tetrasubstituted double bond. Furthermore, in the spectrum there were the signals of four methyls (δ 12.1, 18.7, 20.5 and 20.9 ppm), five methylenes (δ 29.0, 31.6, 31.8, 34.3 and 40.1 ppm), two methines (δ 27.2 and 40.3 ppm) and finally two quaternary carbon signals at δ 54.3 and 54.9 ppm. The ¹H NMR spectrum confirmed the presence of the unsaturated aldehyde by signals at δ 9.31 and 6.82 ppm. The four methyls appeared as two singlets (δ 1.00 and 1.15 ppm) and two doublets (δ 1.01 and 1.03 ppm). The combined use of H-H COSY and HMQC evidenced the presence of three spin systems (Figure 1). These fragments were connected by HMBC correlations between H-2 protons (δ 2.90-3.05 ppm) and C-9 (δ 54.9 ppm) and C-17 (δ 12.1 ppm), H-17 (δ 1.15 ppm) and C-2 (δ 40.1 ppm), C-9 (δ 54.9 ppm) and C-1 (δ 211.2 ppm), between H-16 (δ 1.00 ppm) and C-7 (δ 29.0ppm), C-6 (δ 54.3 ppm), C-14 (δ 221.7 ppm), H-13α (δ 3.35 ppm) and C-15 (δ 193.1 ppm) (Figure 1).

All these data allowed us to identify compound 1 as 1-oxo-cyathin B₂ [5,6]. The relative stereochemistry of cyrneine E was deduced from NOESY correlations (Figure 2).

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/RNP

References


ACG publications

© 2013 Reproduction is free for scientific studies