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A depside from *Frullania trichodes* Mitt.

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ABSTRACT

*Chemical investigation of the dichloromethane extract of Frullania trichodes Mitt.led to the isolation of atranorin (**1**). The structure of **1**was elucidated by extensive 1D and 2D NMR spectroscopy and confirmed by comparison of its ^{1}H and ^{13}C NMR data with those reported in the literature.*

Keywords: *Frullania trichodes* Mitt., Frullaniaceae, liverwort, atranorin

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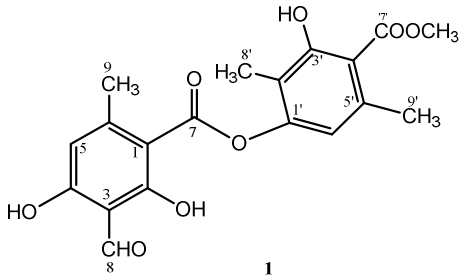
INTRODUCTION

Frullania trichodes Mitt.(syn. *Frullania vethii* Sande Lac.)is a Bryophyte which belongs to a group of simple plants called liverworts [1].There are no reported chemical constituents and biological activities of *F. trichotoma.* However, its synonym *F. vethii* was reported to afford guianolides and elemane type sesquiterpene lactones, as well as a large amount of 5-hydroxy-7,4'-dimethoxyflavone [2, 3]. Liverworts of the genus *Frullania* have also been studied chemically. Two new cadinane-type sesquiterpenes, frullanic acid and frullanic acid methyl ester, together with four known bibenzyls, brittonin B, 3,3'-dimethoxy-4,5-methylenedioxybibenzyl, 3,4,5,3',4'-pentamethoxybibenzyl and 3-(4'-methoxybenzyl)-5,6-dimethoxyphthalide, were isolated from the Chinese liverwort *F. serrata* [4].Another liverwort, *F. brasiliensis*affordedtwo eremophilanes, 5-epi-dilatanolide A [5] and 5-epi-dilatanolide B [5] and two eudesmanes, (+)-frullanolide [5] and nepalensolide A [6].The Indian *F. inflata*was reported to contain the sesquiterpenes, (11S)-11,13-dihydrolipiferolide, α-cubebene, β-cubebene, α-copaene, β-caryophyllene, germacrene-A, α-selinene, β-selinene and β-guaiene [7]. Another study reported the isolation of tamariscene, valerena-4,7(11)-diene, pacifigorgia-1,10-diene, pacifigorgia-1(6),10-diene, pacifigorgia-1(9),10-diene, pacifigorgia-2,10-diene, and pacifigorgia-2(10),11-diene from *F. tamarisci*, *F. fragilifolia*and *Valeriana officinalis* [8]. In another study, *F. muscicola* yielded stigmasterol arachidate, sitosterol, apigenin-7,4'-dimethy ether, scutellarin-6,4'-dimethyl ether, 6-hydroxyluteolin-6,3'-dimethyl ether, scutellarin-6-methyl ether, and daucosterol[9]. Furthermore, *ent*-labdane type diterpenoid, muscicolone, two bibenzyls and four flavonoids were isolated from the liverwort *F. muscicola* Steph. [10]. Muscicolone showed cytotoxic effects to some human tumor cells [10]. A new pacifigorgiane sesquiterpenoid alcohol, tamariscol was isolated from another liverwort *F. tamarisci* [11]. The diterpenoids, 1,2-dehydro-3,7-dioxo-manoyl oxide, 1,2-dehydro-7β-hydroxy-3-oxo-manoyl oxide, 3,7-dioxo-manoyl oxide, 3-β-hydroxy-7-oxo-manoyl oxide and highly methoxylated bibenzyls were isolated from the *F. inouei* [12].

We report herein the isolation of atranorin (**1**) from *F. trichodes* Mitt. To the best of our knowledge this is the first report on the isolation of **1** from *F. trichodes.*



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MATERIALS AND METHODS

General Experimental Procedure

NMR spectra were recorded on a Varian VNMRS spectrometer in $CDCl_3$ at 600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR spectra. Column chromatography was performed with silica gel 60 (70-230 mesh). Thin layer chromatography was performed with plastic backed plates coated with silica gel F_{254} and the plates were visualized by spraying with vanillin/H_2SO_4 solution followed by warming.

General Isolation Procedure

A glass column 12 inches in height and 0.5 inch internal diameter was used for the chromatography of the crude extract. Two milliliter fractions were collected. All fractions were monitored by thin layer chromatography. Fractions with spots of the same R_f values were combined and rechromatographed in appropriate solvent systems until TLC pure isolates were obtained. Final purifications were conducted using Pasteur pipettes as columns. One milliliter fractions were collected.

Plant material

The samples were found growing on palm tree trunks with direct sunlight exposure in the town of Banaue, Ifugao Province, Cordillera Administrative Region, Philippines. The sample location is N 16°55.607', E 121°03.199' at about 1350 meters above sea level. The area endures mountain climate with temperatures at the time of collection about 10-15°C, and frequent fog. Samples were collected on January 9, 2016. The liverwort was identified as *Frullania trichodes* Mitt. by Virgilio C. Linis of the Biology Department, De La Salle University, Manila, Philippines.

Isolation

The air-dried *F. trichodes* (0.80 g) was ground in an osterizer, soaked in CH_2Cl_2 for three days, and then filtered. The filtrate was concentrated under vacuum to afford a crude extract (0.59 g) which was chromatographed using increasing proportions of acetone in CH_2Cl_2 (10% increment) as eluents. The 70% to 90% acetone in CH_2Cl_2 fractions were combined and rechromatographed (2 ×) using CH_3CN:Et_2O:CH_2Cl_2 (2.5:2.5:5, v/v) to yield **1** (5 mg) after washing with petroleum ether, followed by Et_2O.

Atranorin(**1**):^1H NMR(600 MHz, $CDCl_3$): δ6.38 (s, H-5), 10.34 (s, H-8), 2.67 (s, CH_3-9), 6.50 (s, H-6'), 2.07 (s, CH_3-8'), 2.53 (s, CH_3-9'), 3.97 (s, OCH_3) 12.48 (s, 2-OH), 12.53 (s, 4-OH), 11.93 (s, 3'-OH);^{13}C NMR(150 MHz, $CDCl_3$):δ102.82 (C-1), 169.08 (C-2), 108.53 (C-3), 167.47 [C-4], 112.84 (C-5), 152.43 (C-6), 169.69 (C-7), 193.83 (C-8), 25.57 (C-9), 151.96 (C-1'), 116.77 (C-2'), 162.87 (C-3'), 110.24 (C-4'), 139.86 (C-5'), 115.79 (C-6'), 172.17 [C-7'), 9.41 (C-8'), 24.02 (C-9'), 52.33 (OCH_3).

RESULTS AND DISCUSSION

Silica gel chromatography of the dichloromethane extract of *Frullania trichodes* led to the isolation of atranorin (**1**). The structure of **1** was elucidated by extensive 1D and 2D NMR spectroscopy and confirmed by comparison of its ^1H and ^{13}C NMR data with those reported in the literature]13].

Atranorinis found in a variety of lichen species. It exhibited anti-proliferative action against malignant cell lines [14], antinociceptive effects [15, 16] and antibiotic action against *M. aurum* [17]. It was found to inhibit leukotriene B4 synthesis in leukocytes, which might affect inflammatory processes [18]and modulates the wound healing process [19].

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