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Original Article

A Triterpene and a Depside from *Parmotrema austrocetratum* Elix and J. Johnst.

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ABSTRACT

Introduction: *Parmotrema austrocetratum* Elix and J. Johnst. (syn. *Rimelia austrocetrata* Elix and J. Johnst.) which belongs to a large genus of lichenized fungi, *Parmotrema* Massalongo under family Parmeliaceae was investigated for its chemical constituents. **Methods:** The compounds were isolated by silica gel chromatography and their chemical structures were elucidated by NMR spectroscopy. **Results:** Chemical investigation of the dichloromethane extract of *Parmotrema austrocetratum* Elix and J. Johnst. has led to the isolation of zeorin (**1**) and atranorin (**2**). **Conclusion:** *P. austrocetratum* shares similar chemical characteristic with other *Parmotrema* species which afforded atranorin. This work highlights the first reported isolation of **1** from *P. austrocetratum* and the genus *Parmotrema*.

Key words: *Parmotrema austrocetratum*, *Rimelia austrocetrata,* Parmeliaceae, Zeorin, Atranorin.

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INTRODUCTION

Parmotrema austrocetratum Elix and J. Johnst. (syn. *Rimelia austrocetrata* Elix and J. Johnst.) belongs to a large genus of lichenized fungi under family Parmeliaceae.[1] Thallus of *P. austrocetratum* are loosely adnate with broad, rotund lobe apices. The upper surface is reticulately cracked, maculae forming areoles, then eventually flaking off to expose the medulla. Erhizinate marginal in the lower cortex are either absent or very narrow. Lower cortex generally black with brown marginal area Soredia are absent. Marginal cilia frequent while rhizines are simple to squarrose and black in color.[1] Its genus name *Parmotrema* refers to the perforate apothecia (Greek parmos = cup and trema = perforation).[2] In the Philippines, *P. austrocetratum* is distributed in Northern Cordillera in Luzon island and Mount Apo in Mindanao island.[3-4] The Philippine specimen chosen for our chemical investigation was gathered from the trunk of a Benguet pine (*Pinus kesiya* Royle ex Gordon) in Camp John Hay, Baguio City.

Parmotrema austrocetratum was reported to contain atranorin and salazinic acid.[1] Of relevance to our present report are several studies on the genus *Parmotrema* which reported the presence of atranorin in *P. arnoldii*,[5] *P. crinitum*,[5] *P. perlatum*,[5] *P. stuppeum*,[5] *P. crocoides*,[6] *P. dilatatum*,[6] *P. eciliatum*,[6] *P. endosulphureum*,[6] *P. erubescens*,[6] *P. flavescens*,[6] *P. flavomedullosum*,[6] *P. gardneri*,[6] *P. latissimum*,[6] *P. eucosemothetum*,[6] *P. masonii*,[6] *P. mellissii*,[6] *P. neotropicum*,[6] *P. permutatum*,[6] *P. robustum*,[6] *P. rubifaciens*,[6] *P. subarnoldii*,[6] *P. subisidiosum*,[6] *P. subsumptum*,[6] *P. wrightii*,[6] *P. sancti-angeli*,[6] *P. simulans*,[6] *P. sorediiferum*,[6] *P. soredioaliphaticum*,[6] *P. hydrium*,[7] *P. praesorediosum*,[8] *P. rampoddense*,[8] *P. tinctorum*,[8-9] *P. reticulatum*,[8] *P. negrosorientalum*,[4] *P.* lichexanthonicum,[10] *P. cetratum*,[11] *P. cristiferum*,[11] *P. defectum*,[11] *P. grayanum*,[11] *P. margaritatum*,[11] *P. perlatum*,[11] *P. pseudocrinitum*,[11] *P. reticulatum*,[11] *P. subtinctorium*.[11]

We report herein the isolation of zeorin (**1**) and atranorin (**2**) (Figure 1) from *P. austrocetratum*. To the best of our knowledge this is the first report on the isolation of **1** from *P. austrocetratum* and the genus *Parmotrema*.

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.

Sample Collection

The Philippine specimen chosen for our chemical investigation was gathered from the trunk of a Benguet pine (*Pinus kesiya* Royle ex Gordon) in Camp John Hay, Baguio City (date of collection: 14 October 2017).

Isolation of the Chemical Constituents of P. austrocetratum

The freeze-dried *P. austrocetratum* (17.52 g) was ground in a blender, soaked in CH_2Cl_2 for three days and then filtered. The filtrate was concentrated under

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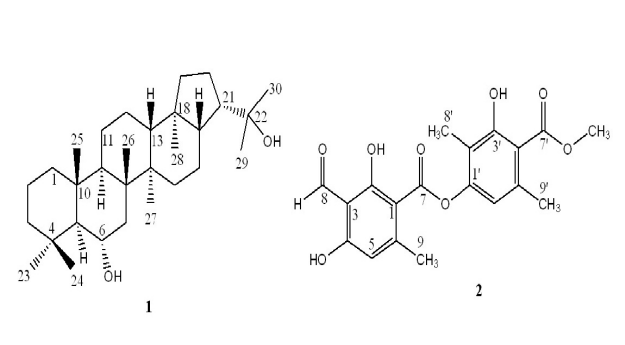

Figure 1: Chemical structures of zeorin (**1**) and atranorin (**2**).

vacuum to afford a crude extract (0.1578 g) which was chromatographed by gradient elution using petroleum ether, 2.5% EtOAc in petroleum ether, 5% EtOAc in petroleum ether, 7.5% EtOAc in petroleum ether, 10% EtOAc in petroleum ether, 12.5% EtOAc in petroleum ether, 15% EtOAc in petroleum ether, CH_2Cl_2, CH_3CN:Et_2O:CH_2Cl_2 (0.5:0.5:9, v/v), CH_3CN:Et_2O:CH_2Cl_2 (1:1:8, v/v), CH_3CN:Et_2O:CH_2Cl_2 (2:2:6, v/v). The CH_3CN:Et_2O:CH_2Cl_2 (0.5:0.5:9, v/v) fraction was rechromatographed using 15% EtOAc in petroleum ether, followed by CH_3CN:Et_2O:CH_2Cl_2 (0.5:0.5:9, v/v). The fractions eluted with 15% EtOAc in petroleum ether were combined and rechromatographed using the same solvent to afford **1** (4.3 mg) after washing with petroleum ether. The fractions eluted with CH_3CN:Et_2O:CH_2Cl_2 (0.5:0.5:9, v/v) were combined and rechromatographed using the same solvent to yield **2** (15.1 mg) after washing with petroleum ether.

Zeorin (**1**): ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.74 (s, CH_3-28), 0.85 (s, CH_3-25), 0.96 (s, CH_3-27), 1.00 (s, CH_3-26), 1.02 (s, CH_3-23), 1.13 (s, CH_3-24), 1.16, 1.19 (s, CH_3-29, CH_3-30), 3.94 (dt, *J* = 4.2, 10.8 H-z); ^{13}C NMR (150 MHz, $CDCl_3$): δ 40.33 (C-1), 18.50 (C-2), 43.79 (C-3), 33.60 (C-4), 61.07 (C-5), 69.30 (C-6), 45.48 (C-7), 42.85 (C-8), 49.41 (C-9), 39.33 (C-10), 21.03 (C-11), 23.98 (C-12), 49.77 (C-13), 41.86 (C-14), 34.32 (C-15), 21.90 (C-16), 53.94 (C-17), 43.99 (C-18), 41.21 (C-19), 26.58 (C-20), 51.05 (C-21), 73.90 (C-22), 36.73 (C-23), 22.10 (C-24), 17.11 (C-25), 18.25 (C-26), 17.05 (C-27), 16.07 (C-28), 28.75 (C-29), 30.87 (C-30).

Atranorin (**2**): ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.38 (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), 11.92 (s, 3'-OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ 102.82 (C-1), 169.07 (C-2), 108.53 (C-3), 167.47 (C-4), 112.84 (C-5), 152.42 (C-6), 169.68 (C-7), 193.82 (C-8), 25.56 (C-9), 151.97 (C-1'), 116.77 (C-2'), 162.86 (C-3'), 110.24 (C-4'), 139.85 (C-5'), 116.00 (C-6'), 172.18 [C-7'), 9.35 (C-8'), 24.01 (C-9'), 52.32 (OCH_3).

RESULTS AND DISCUSSION

Silica gel chromatography of the dichloromethane extract of *P. austrocetratum* has led to the isolation of zeorin (**1**) and atranorin (**2**). The structures of **1** and **2** were elucidated by extensive 1D and 2D NMR spectroscopy and confirmed by comparison of their NMR data with those reported in the literature for zeorin[12-13] and atranorin,[14] respectively.

Although there is no reported biological activity for *P. austrocetratum*, the compounds isolated from the plant were reported to possess diverse activities. Zeorin (**1**) and atranorin (**2**) have shown antidiabetic and antioxidant activities.[15] Triterpene **1** also showed strong activity against bacteria and fungi.[16] Depside **2** exhibited anti-proliferative action against malignant cell lines,[17] antinociceptive effects[18-19] and antibiotic action against *M. aurum*.[20] It was found to inhibit leukotriene B4 synthesis in leukocytes, which might affect inflammatory processes[21] and modulates the wound healing process.[22]

CONCLUSION

P. austrocetratum shares similar chemical characteristic with other *Parmotrema* species which yielded atranorin. This study highlights the first reported isolation of **1** from *P. austrocetratum* and the genus *Parmotrema*.

ACKNOWLEDGEMENT

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATIONS

CH_2Cl_2: Dichloromethane; **CH_3CN:** Acetonitrile; **EtOAc:** Ethyl acetate; **Et_2O:** Diethyl ether.

SUMMARY

Chemical investigation of the dichloromethane extract of *Parmotrema austrocetratum* Elix and J. Johnst. has led to the isolation of a triterpene, zeorin (**1**) and a depside, atranorin (**2**). The structures of **1** and **2** were elucidated by 1D and 2D NMR spectroscopy and confirmed by comparison of their NMR data with literature data.

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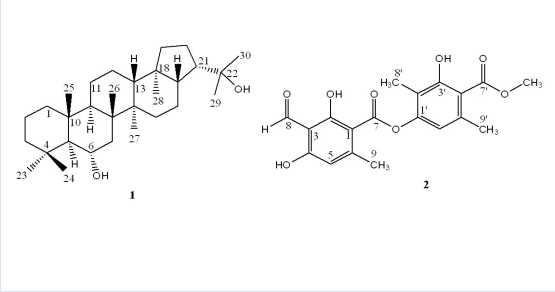
GRAPHICAL ABSTRACT



SUMMARY

- Chemical investigation of the dichloromethane extract of *P. austrocetratum* has led to the isolation of zeorin (1) and atranorin (2). This is the first report on the isolation of 1 from *P. austrocetratum* and the genus *Parmotema*.

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