
SHORT REPORTS

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THE MAJOR CONSTITUENTS OF TWO LICHENS - *CALOPLACA FULGENS* AND *SIPHULA CORIACEA*

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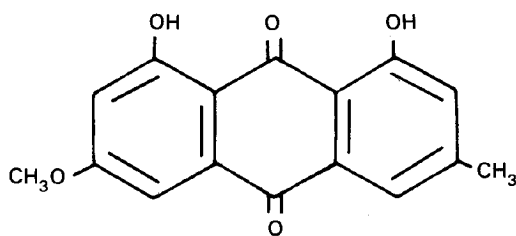
Abstract

The major constituents of Caloplaca fulgens Koerb and Siphula coriacea Tayl. ex Nyl. have been identified as parietin (1) and barbatic acid (2), respectively.

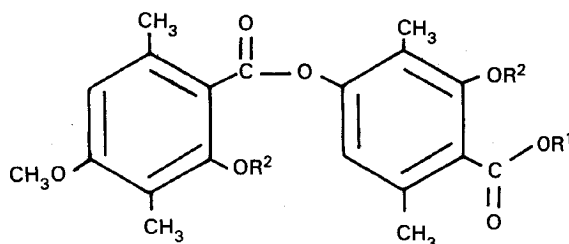
In a limited investigation of two common Western Australian lichens, which do not appear to have been examined previously, we have identified parietin (1) as the major constituent of the crustose lichen *Caloplaca fulgens* Koerb. This anthraquinone (1), which is also known as physcion, has been encountered frequently in other *Caloplaca* species.¹

Two ecotypes of the fruticose lichen *Siphula coriacea* Tayl. ex Nyl. have given high yields of barbatic acid (2) which was characterized by conversion into its methyl ester (3) and into methyl *O*-methyldiffractate (4).

The last finding is of some practical value for it has since been exploited by other workers^{2,3} who have used the barbatic acid (2) from this source as a convenient starting material for the synthesis of other lichen metabolites.



(1)

(2) $R^1 = H, R^2 = H$ (3) $R^1 = CH_3, R^2 = H$ (4) $R^1 = CH_3, R^2 = CH_3$

Melting points were determined on a Kofler hot stage, except in the case of parietin. Nuclear magnetic resonance spectra were measured with a Varian A60-A spectrometer operating at 60 MHz. The mass spectra were determined with a Varian MAT-CH7 instrument. Light petroleum refers to a fraction of boiling range 55–65°. Voucher specimens of the lichens have been deposited in the Herbarium of the Department of Botany (UWA), University of Western Australia.

Isolation of Parietin (1) from *Caloplaca fulgens*

Chlorite-quartz schist rocks (ca. 20 kg), supporting the orange *Caloplaca fulgens* (UWA 546) and a black unidentified *Catillaria* species were collected on the sea shore near East Mount Barren and immersed in acetone overnight at room temperature. The extract was decanted and evaporated then the benzene-soluble portion of the residue was crystallized from ethyl acetate and sublimed (180–210°/2 mm). Crystallization of the sublimate from ethyl acetate yielded parietin (1) as orange needles (245 mg) m.p. 208–210° (sealed capillary) (lit⁴ 206–207°). N.m.r. δ (CDCl₃): 2.47, s, 3, CCH₃; 3.94, s, 3, OCH₃; 6.70, d (J = 2.5 Hz), 1, ArH; 7.10, s(b), 1, ArH; 7.48, d (J = 2.5 Hz), 1, ArH; 7.64, s(b), 1, ArH; 12.13, s, 1, OH; 12.32, s, 1, OH. Mass spectrum (110°/70 eV) m/e: 284 (100%), 255 (6), 241 (6), 227 (4), 213 (4), 185 (5), 128 (6).

No parietin (1) could be detected by thin layer chromatography in the acetone extract of a small amount of the *Catillaria* species which had been scraped from the rock.

Isolation of Barbatic Acid (2) from Siphula coriacea

(i) The lichen (UWA 670, 405 g), which was collected from a granite outcrop 28 miles from Perth on the road to Brookton, was milled and percolated with ether. Concentration of the extract gave crude barbatic acid (2) (65.4 g) which crystallized from methanol as needles (51.4 g) m.p. 189–190.5° or from acetone as prisms m.p. 190–191° (lit⁵ 186–187°). N.m.r. δ ((CD₃)₂ SO and CDCl₃) : 2.10, s, 6, CCH₃; 2.59, s, 3, CCH₃; 2.69, s, 3, CCH₃; 3.90, s, 3, OCH₃; 6.41, s, 1, ArH; 6.52, s, 1, ArH; 11.92, s, 1, OH; 12.8–13.2, s(b), 1, OH. Mass spectrum (90°/70 eV) m/e: 360 (3%), 182 (9), 180 (12), 179 (100), 178 (10), 164 (17), 150 (7), 138 (9), 137 (9), 136 (25), 135 (6), 123 (6), 107 (10).

(ii) A smaller ecotype of this lichen (UWA 2224, 120 g) which was collected from a granite sheet 260 miles from Perth on the road to Kalgoorlie, was extracted as before. The crude barbatic acid (2) (15.3 g) crystallized from benzene as needles (12.4 g) m.p. 189–190°, not depressed on admixture with the sample obtained above.

Methyl barbatate (3) and Methyl O-methylidiffractate (4)

(i) Treatment of barbatic acid (2) (1.0 g) in acetone (50 ml) with excess ethereal diazomethane afforded methyl barbatate (3) as needles m.p. 171–172° (lit⁵ 173°). N.m.r. δ (CDCl₃) : 2.10, s, 6, CCH₃; 2.56, s, 3, CCH₃; 2.69, s, 3, CCH₃; 3.91, s, 3, OCH₃; 3.98, s, 3, OCH₃; 6.41, s, 1, ArH; 6.53, s, 1, ArH; 11.92, s, 1, OH; 12.33, s, 1, OH.

(ii) A solution of barbatic acid (2) (10 g) in dry acetone (1 l) was stirred with anhydrous K₂CO₃ (23 g) and dimethyl sulfate (11 g) at room temperature for 24 h. When the mixture was worked up in the usual way methyl O-methylidiffractate (4) was obtained; this substance (4) crystallized from light petroleum as needles m.p. 105–106.5° (lit⁶ 106–107°). N.m.r. δ (CCl₄) : 2.10, s, 3, CCH₃; 2.15, s, 3, CCH₃; 2.28, s, 3, CCH₃; 2.42, s, 3, CCH₃; 3.78, s, 6, OCH₃; 3.80, s, 3, OCH₃; 3.85, s, 3, OCH₃; 6.42, s, 1, ArH; 6.72, s, 1, ArH.

Acknowledgement

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บทคัดย่อ

ส่วนประกอบใหญ่ของ *Caloplaca fulgens* Koerb และ *Siphula coriacea* Tayl. ex Nyl. จากการศึกษพบว่าเป็นพาริติน (1) และกรดบารบาติก (2) ตามลำดับ