

Coumarin Glycosides from the Mosses *Dendroligotrichum dendroides* and *Dawsonia superba**

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*Dedicated to Professor Robert Hegnauer, Leiden,
on the occasion of his 80th birthday*

Mosses, Polytrichales, *Dendroligotrichum dendroides*,
Dawsonia superba, 5, 7, 8-Trihydroxy-coumarin-5-
glucoside derivatives

Dendroligotrichum dendroides and *Dawsonia superba*, which belong to two exclusively Gondwanalandic genera of the Polytrichales, accumulate the same type of coumarins as species of the cosmopolitan genera of that order. The structures of the isolated compounds, one of which is a new natural product, were elucidated spectroscopically.

Introduction

A chromatographic study by Jung (1993) suggested that species of the Polytrichales are chemically characterized by the accumulation of tri- and tetrahydroxycoumarin derivatives. In the case of representative species from the almost cosmopolitan genera *Atrichum*, *Oligotrichum*, *Pogonatum*, and *Polytrichum* this has been verified by the isolation of pure compounds and elucidation of their structures (Jung *et al.*, 1994 and Raubuch, 1998). In this communication we shall report the isolation and identification of trihydroxycoumarin derivatives from *Dendroligotrichum dendroides* and *Dawsonia superba*, representatives of two polytrichalean genera with an exclusive Gondwanalandic distribution.

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Results and Discussion

D. dendroides yielded as its main coumarin 5, 8-dihydroxy-7-methoxycoumarin-5- β -D-glucopyranoside (**1**). This compound occurs also in all Polytrichaceae that have been studied so far (Jung *et al.*, 1994 and Raubuch, 1998). It was identified by its NMR spectra and a chromatographic comparison with authentic material. Further constituents of this moss could not be identified, because we had only a very small sample at our disposition.

For the same reason *D. superba* yielded also only its main coumarin in a quantity that was sufficient for NMR-analysis. It turned out to be a new compound – 5, 7, 8-trihydroxycoumarin-5, 7-di- β -D-glucoside (**2**). This structure was deduced by comparison of its ¹H- and ¹³C-NMR spectra with published data of related compounds and some NOE-experiments (c.f. Jung *et al.*, 1994 and 1995). The multiplicities and chemical shifts of its ¹H as well as ¹³C resonances in the “aromatic range” indicated that **2** is a 5, 7, 8-trihydroxycoumarin derivative. The signals in the “sugar range” revealed that **2** contains two β -glucopyranoses, which are both linked directly to the aglycone, NOE interactions between H-6 and the anomeric protons of both glucoses proved that these sugars are linked to O-5 and O-7. Thus **2** is 3, 7, 8-trihydroxycoumarin-5, 7-di- β -D-glucopyranoside. (Table I).

Although the samples of both species were too small to isolate and identify the minor coumarins, the present results reveal nevertheless that the ability to synthesize trihydroxycoumarins must have existed in the ancestral stock of the Polytrichales before the breaking up of Pangaea.

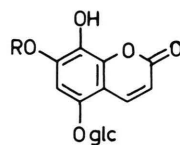
Experimental

The plant material was gathered in New Zealand by permission of the local authorities.

Dendroligotrichum dendroides (Hedw.) Broth. was collected in spring 1994 on the slopes of Mount Taranaki at 900 m s. m. by M. Veit; a voucher is kept in the private herbarium of H. G. (R 289) *Dawsonia superba* Grev. was collected by S. Bloor in January 1990 in Westland; a voucher is deposited at CHR (No. 465120).

Extraction and isolation were performed as described previously (Jung *et al.*, 1994 and 1995). By





1: R=CH₃

2: R=glc

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Table I. ¹³C- and ¹H-NMR data of **2** recorded in DMSO-d₆ at ambient temperature with 100 and 400 MHz respectively.

¹³ C ¹ H Position	¹³ C	¹ H
2	159.9	-
3	111.4	6.24 d (9.6)
4	139.4	8.20 d (9.6)
5	145.8	-
6	98.7	6.85 s
7	148.2	-
8	128.3	-
9	142.5	-
10	104.7	-
1', 1''	100.9, 100.9	4.86 d (7.5), 4.82 d (7.4)
2', 2''	73.1, 73.1	3.74–3.10 m, 3.74–3.10 m
3', 3''	76.1, 76.8	3.74–3.10 m, 3.74–3.10 m
4', 4''	69.9, 69.9	3.74–3.10 m, 3.74–3.10 m
5', 5''	76.9, 76.9	3.74–3.10 m, 3.74–3.10 m
6', 6''	60.9, 60.9	3.74–3.10 m, 3.74–3.10 m

these methods 3 g branchlets of *D. dendroides* yielded 2 mg **1** and 38 g gametophytes of *D. su-perba* gave 7 mg **2**.

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