Phytochemistry, 1978, Vol 17, pp 503–504 Pergamon Press. Printed in England

LIGNIN OF 'GIANT' MOSSES AND SOME RELATED SPECIES

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(*Received* 12 *September* 1977)

Key Word Index—*Dawsonia*; *Polytrichum*; Bryophyta; Musci; Polytrichales; giant mosses; lignin; phenolic polymers.

Abstract—A number of mosses exhibiting gigantism, mainly belonging to the genus *Dawsonia*, have been investigated for the presence of lignin by oxidative degradation. They were found to be devoid of lignin but contain another type of phenolic cell wall material.

INTRODUCTION

The question about the presence of lignin in bryophytes has considerable phylogenetic interest. Only very recently, relevant experimental evidence has accumulated indicating that there is no lignin in bryophytes [1–4]. Instead mosses and liverworts contain one of several types of non-lignin polyphenols [2, 3].

One problem that was left for further investigation is that of the occurrence of lignin in the 'giant' mosses of Australasia, i.e. a number of erect-growing members of the order *Polytrichales* (*Musci*) [5] belonging to the genera *Polytrichum and Dawsonia*. Most of the species exhibiting gigantism pertain to the genus *Dawsonia*, recently reviewed by van Zanten [6]. Some of these have been claimed to contain lignin [7, 8], or at least phenolic material [9], which might account for their ability to grow to a considerable height. Recent histochemical studies by Hébant [1], on the other hand, have not substantiated these claims. Furthermore, the results of chemical investigations on two related species, *Polytrichum commune* and *Pogonatum urnigerium*, have shown that at least these *Polytrichales* have no lignin [3]. The literature about the occurrence of lignin in mosses and liverworts has very recently been reviewed [10].

The aim of this paper is to present some results concerning the presence of lignin and polyphenols in a number of 'giant' mosses. They were obtained by chemical characterization using a method for degradation [11] which involves heating the plant material with aqueous NaOH–Na_2S. The solubilized material containing lignin and/or polyphenols is methylated and oxidized ($KMnO_4$–$NaIO_4$ in aqueous NaOH, then H_2O_2 in aqueous Na_2CO_3) to yield a mixture of aromatic carboxylic acids, the major components of which are estimated as Me esters by GLC. Knowledge of their structures and relative composition suffices for a broad characterization of the biopolymer—lignin or a non-lignin polyphenol—they are derived from.

RESULTS AND DISCUSSION

The yields of 5 major Me esters from the oxidative degradation are given in Table 1. They were found in comparable amounts in all species. Esters **1** (Me veratrate), **2** (diMe isohemipate) and **3** (diMe metahemipate) could be derived from lignin. This origin is however excluded by the absence of both 3′,4,5-trimethoxy-3,4′-oxydibenzoate and dimethyl 5,5′-dehydro-diveratrate, which are always obtained from lignins containing the respective precursor structures ultimately derived from coniferyl alcohol. The claims of Siegel and others that giant mosses contain or might contain lignin are thus refuted also on basis of chemical evidence.

Table 1. Yields of Me esters obtained by oxidative degradation of some *Polytrichales*, including several species exhibiting gigantism ('giant' mosses), in mg/g plant material

Species	Ester yield					Material
	1	2	3	4	5	
Dawsonia grandis	4 7	0 7	2 5	1 2	0 9	gametophytic stems
*D. longiseta**	8 7	0 8	2 0	2 0	1 5	seta
*D papuana**	6 3	1 1	4 1	2 5	1 3	gametophytic stems
D polytrichoides	4 7	0.4	3 0	0 6	1 2	gametophytic stems
*D superba**	6 1	0 9	4 1	1.7	0.9	gametophytic stems
*Dendroligotrichum dendroides**	8 1	0 8	4 1	4 9	4 1	gametophytic stems
Polytrichadelphus magellanicus	5.1	1 3	2 8	1 2	0 6	gametophytic stems
Polytrichum commune†	7 8	1 5	2.2	19	4 5	gametophytic stems

*Mean of yields of two oxidative degradations.
†*Polytrichum commune* Hedw., cited from ref. [3].

The dibenzofurans **4** (Me 4,7,9-trimethoxy-2-dibenzofurancarboxylate) and **5** (Me 3-(4,7,9-trimethoxy-2-dibenzofuranyl)-propanoate) are, as well as compounds **1–3**, degradation products of non-lignin cell wall polyphenols that seem to be shared by all members of the *Polytrichaceae*, as well as by at least some other bryophytes [3]. The present results are also in accordance with the aforementioned investigations by Hébant with the Wiesner reaction specific for coniferyl alcohol-derived substructures of the coniferaldehyde type in lignins.

The hydroids of both sporophytes [12] and gametophytes [13] in *Dawsonia* and *Polytrichum* are devoid of a protoplast and have partially hydrolyzed end walls. Their water-conducting properties point to a considerable functional similarity with tracheids in higher plants. Protection of their lateral walls against hydrolysis has been explained by the presence of polyphenols [14].

It should be noted that the central strand of hydroids possess a middle lamella. Under the electron microscope the cell corners in contrast to the cell wall show an amorphous structure [15]. The same is true for cell corners in lignified cell of higher plants [16], where the middle lamella and the cell corners are mainly made up by lignin [17]. Scanning UV-microscopy of hydroids in thin stem sections should reveal if this suggested distribution of moss polyphenols is correct. The function of polyphenolic material in bryophytes may thus be similar to that of lignin in higher plants, although its success in conferring rigidity to the moss stem is rather limited.

EXPERIMENTAL

Plant material (see also Table 1). Fr. or air-dried (dry) plant material was provided by Dr. Ch. Hébant, Univ. Montpellier, France (Hé.). Dr. G. A. M. Scott, Monash Univ., Vic., Australia (Sc.) and Dr. B. O. van Zanten, Biological Centre, Haren, the Netherlands (v. Za.). *Dawsonia grandis* Schlieph. & Geh. (fr., New Guinea, v. Za); *D. longiseta* Hamp. (dr., South-East Australia, Sc.); *D. papuana* F. Muell. ex Schlieph. & Geh. (fr., New Guinea, v. Za.); *D. polytrichoides* R Brown (fr., Eastern Australia, v. Za.); *D. superba* Grer. var. *superba* (Wijk) Zant (dr., New Zealand, Hé.): *Dendroligotrichum dendroides* (Hedw.) Broth. (dr., New Zealand, Hé.), *Polytrichadelphus magellanicus* (Hedw.) Mitt. (dr., New Zealand, Hé.). Gametophytic stems of the respective moss were freed of leaves, killed with EtOH, if fr. suspended in toluene and ground in a vibrating mill with ceramic cylinders to pass a 240 mesh sieve. The resulting meal was extracted and subjected to oxidative degradation as previously described [11].

Acknowledgements—The plant material used in this study was generously provided by Dr. B. O. van Zanten, Dr. G. A. M. Scott and Dr. Ch. Hébant, who also contributed to this paper by valuable suggestions.

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