δ2·95, 2H, double doublet at δ2·54 (*J* 16 Hz) and at δ3·03 (*J* 16 Hz)) and four aromatic protons (AA'XX' type quartet at δ6·67–7·15).

The compound formed a dimethyl ester by treatment with $CH_2N_2$ for 30 min in $Et_2O$, which was purified by silica gel column chromatography to give a light yellow oil; MS (*m/e*): 268 (Calc. for $C_{13}H_{16}O_6$, $M^+$), 250, 218, 209, 191, 177, 161, 135, 107, 101, 77, IR $\nu_{max}$ (film) $cm^{-1}$: 3400–3200 (OH), 1750–1730 (COOMe). NMR ($CDCl_3$): δ2·65 (1H, *d*, *J* 16 Hz), 2·92 (2H, *s*), 3·10 (1H, *d*, *J* 16 Hz), 3·69 (3H, *s*, OMe), 3·76 (3H, *s*, OMe), 6·6–7·15 (4H, AA'XX''). Complete methylation with $CH_2N_2$ in MeOH (24 hr) gave a dimethyl ester monomethyl ether after silica gel column chromatography, as a pale yellow oil; MS (*m/e*): 282 (Calc. for $C_{14}H_{18}O_6$, $M^+$), 264, 223, 191, 149, 135, 121, 101, 91, 77. NMR ($CDCl_3$): δ2·65 (1H, *d*, *J* 16 Hz), 2·93 (2H, *s*), 3·05 (1H, *d*, *J* 16 Hz), 3·67 3·75, 3·79 (each 3H, *s*, OMe), 6·74–7·20 (4H, AA'XX'). IR $\nu_{max}$(film) $cm^{-1}$: 3500–3400 (OH). 1740 (COOMe).

From this data the isolated compound was considered to be 2-(4-hydroxy-benzyl)malic acid, and this was confirmed by comparison of IR, NMR, and MS data with those reported by Harris *et al.*[1].

*Biological significance.* The auxin-like activity was tested with oat coleoptiles (5 mm sections cut 3 mm below the tip), 20 sections per dish floated on 1 ml of the test solutions. The relative mean length of sections in various concentrations of the compound (in parenthesis) to that of the control was: 88% (1000 ppm), 115% (100 ppm), 108% (10 ppm), 105% (1 ppm), and 132% (IAA, 1 ppm).

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# PHLOROGLUCINOL DERIVATIVES IN *DRYOPTERIS CHRYSOCOMA*

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**Key Word Index**—*Dryopteris chrysocoma*; Polypodiaceae; phloroglucinol derivatives; albaspidin, filixic acid and flavaspidic acid.

In earlier communications, phloroglucinol derivatives of various species of *Dryopteris* from Europe, North America, Africa and Japan have been described [1–5]. The present report on *D. chrysocoma* (Christ) C. Chr., from Himalayas (India), is a part of the same programme. This fern is diploid and has been reported to occur in abundance in some areas of the Himalayas at an altitude of 1·600–2·500 m [6,7]. It is one of the 5 Indian *Dryopteris* species, which are official in the Pharmacopoeia of India (1966) as a source of well known anthelmintic drug male fern [8]. Another fern, *Polystichum squarrosum* (D. Don) Fee, often grows with it. In the present paper, studies on the phloroglucinol derivatives in both of these ferns are reported. Only preliminary chemical work has been done previously on the oleoresin of Indian *Dryopteris* spp. [6,9].

## RESULTS AND DISCUSSION

As is evident from the yield of oleo-resin and crude filicin (Table 1), *D. chrysocoma* is quite rich in phloroglucinol derivatives, whereas *P. squarrosum* is totally devoid of them. The phloroglucinol mixture of the crude filicin was separated by column chromatography on Si gel [1–5] and crystals of various homologues of albaspidin, filixic acid and flavaspidic acid were isolated and studied by MS and TLC.

(a) Albaspidin, mp 142–143°. The MS shows 4 molecular peaks at *m/e* 460 (weak), 446 (weak), 432 and 418 corresponding to albaspidins BB, PB, PP and /or AB and AP, respectively.

(b) Albaspidin, mp 133–134°. The MS shows 3 molecular peaks at *m/e* 460, 446 and 432 (weak) corresponding to albaspidins BB, PB and PP, respectively.

(c) Filixic acid, mp 169–170°. The MS shows 4 molecular peaks at *m/e* 668, 654, 640 and 626 (weak), corresponding to filixic acids BBB, PBB, PBP and/or ABH and ABP, respectively.

(d) Flavaspidic acid, mp 150–152°. The MS shows only one molecular peak at *m/e* 446, which corresponds to flavaspidic acid BB. Both *D. chrysocoma* and *D. filix-mas* resemble each other in having considerable amounts of filixic acid and flavaspidic acid. These species, however, differ in that large amounts of albaspidin occur in *D. chrysocoma* and not in *D. filix-mas*. The latter species contains para-aspidin, desaspidin and trisdesaspidin, not found in *D. chrysocoma* (cf. Table). Investigation of the acylfilicinic acids formed by the reductive alkaline clea-

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Table 1. Composition of the phloroglucinol derivatives in *D. chrysocoma*, *D. filix-mas* and *P. squarrosum*

| Taxon and ploidy | Origin | Dried rhizomes (g) | Oleoresin g | (%) | Crude filicin g | (%) | Albaspidin | Filixic acid | Paraaspidin | Desaspidin | Trisdesaspidin | Flavaspidic acid |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *D. chrysocoma* [2x] | India | 240 | 32 | (13) | 5·3 | (2·2) | ++ | ++ | − | − | − | +++ |
| *D. filix-mas* [4x] | Finland | 733 | 74·8 | (9·8) | 12·7 | (1·8) | − | +++ | + | + | (+) | +++ |
| *P. squarrosum* [2x] | India | 500 | 7·2 | (1·2) | − | − | − | − | − | − | − | − |

Phloroglucinol derivatives in *D. chrysocoma* and *D. filix-mas* exist as mixtures of butyryl (B), propionyl (P), and acetyl (A) homologues (6:3:1) (cf. text). Key:— absent; (+) present in traces (<5%); + present in small amounts (5–10%); + + present in moderate amounts (10–20%); + + + present in large amounts 20%).

vage [3,10] revealed the presence of butyryl (B) (60%), propionyl (P) (30%) and acetyl (A) (10%) homologues in *D. chrysocoma*. Similar percentages were found for *D. filix-mas*.

The presence of filixic acid in *D. chrysocoma* indicates that it is chemotaxonomically related to the taxa of *D. filix-mas* and *D. villarii* complex (cf. Ref. [1]). The high yield of crude filicin, as well as its chemical resemblance to that of *D. filix-mas* confirm its use as a substitute of male fern and justifies its inclusion in Pharmacopoeia of India.

## EXPERIMENTAL

*Plant Material.* Ferns were collected from Simla, Western Himalayas at 1800 m in September 1973. Voucher specimens have been deposited in the Botany Dept. herbarium, University of Helsinki.

*Extraction of rhizomes.* The powdered rhizomes were macerated 3 × with peroxide free ether and crude filicin obtained with MgO, using $Na_2SO_3$ as an antioxidant [1–5]. Yields of oleo-resin ($Et_2O$ extracts) and crude filicins are listed in Table 1.

*Separation of phloroglucinol derivatives.* Crude filicin (5·3 g) was suspended in $C_6H_6$ and chromatographed on a column containing 130 g Si gel. Fractions 1–4 (10 ml each), eluted with $C_6H_6$, contained albaspidin and filixic acid. The residue was crystallised from $Me_2CO$ to give 12 mg albaspidin, mp 142–143°, 4 mg albaspidin mp 134–136°, 11 mg filixic acid mp 169–170° and 17 mg crystalline mixture of filixic acid and albaspidin mp 112–116°. Fractions 5–35 eluted with $C_6H_6$ contained albaspidin, filixic acid and some flavaspidic acid. On cryst. from $Me_2CO$ 2 mg albaspidin mp 133–134° and 17 mg crystalline mixture of albaspidin and filixic acid mp 84–86° were obtained. Fractions 36–95 eluted with $C_6H_6$–$CHCl_3$ (1:1) contained only flavaspidic acid. On cryst. from Me, 34 mg flavaspidic acid BB mp 150–152° and 5 mg more crystals mp 115–120° were obtained. The rest of this fraction (2·15 g) consisted of a brown oil, which did not crystallize.

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# LINDLEYIN, A NEW PHENOLIC GALLYLGLUCOSIDE FROM *AEONIUM LINDLEYI*

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**Key Word Index**—*Aeonium lindleyi*; Crassulaceae; glucoside; lindleyin; 4-(4′-hydroxyphenyl)-2-butanone 4′-*O*-β-D-(6″-*O*-gallyl)glucoside.

In a previous study of *Aeonium lindleyi* W. B., labdane-8α, 15-diol was obtained [1]. The present work reports the isolation of a new phenolic gallylglucoside, named lindleyin, which on the basis of spectral data and