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THE FATTY ACID COMPOSITION OF FERN LIPIDS

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Key Word Index—Ferns; fatty acids; chemotaxonomy; galactosyl diglycerides.

Abstract—Fatty acid compositions of the lipids isolated from the pinnae of four fern species show that they differ from those of the lipids in leaves of higher plants in having C-20 polyunsaturated acids, mainly arachidonic acid. As in higher plants, the ω-3 polyunsaturated acids are concentrated in the monogalactosyl diglycerides. Variations are found both in the fatty acid compositions and in the monogalactosyl/digalactosyl diglyceride ratio during the growing season.

INTRODUCTION

The fatty acid compositions of the lipids in the leaves of higher plants [1–3], conifers [4], and of marine algae [5] have been extensively studied. It has been shown that in all cases the ω-3 acids are concentrated in the galactosyl diglycerides. There is, however, a lack of comparable information for lower land plants such as ferns and mosses, although partial characterizations have been made of the fatty acids of a moss [6], and of three ferns [7].

In the present work, the fatty acid compositions of the pinnae lipids of the ferns *Dryopteris austriaca*, *D. filix-mas*, *Polypodium vulgare* and *Pteridium aquilinum* have been examined and the changes in the fatty acid composition and in the MGDG/DGDG ratio have been investigated in the last named species during the growing season.

RESULTS AND DISCUSSION

The fatty acid composition of the total lipids from the pinnae of 4 fern species are shown in Table 1. The compositions of the lipids from the 4 species are qualitatively similar and resemble those of angiosperms in that the major constituents are linolenic acid (18:3 ω-3), linoleic acid (18:2 ω-6) and palmitic acid (16:0). All 4 species contained considerable amounts of 16:3 ω-3, a lower homologue of linolenic acid and small amounts of 18:3 ω-6 and 18:4 ω-3, both of which are not usually found in angiosperm lipids, but they have been reported in Boraginaceae [2] and Caryophyllaceae [3], and marine algae [5].

The fern lipids differ from those of angiosperms in having various C-20 polyunsaturated acids of which arachidonic acid (20:4 ω-6) is the most abundant (4·3–11·1%) followed by 20:5 ω-3 (0·3–4·0%). C-20 polyunsaturated acids have not so far been reported as constituents of angiosperm leaf lipids, but Nichols [6] reported three 20:4 acids and one 20:5 acid in the lipids of the moss, *Hypnum cupressiforme*. Both C-20 and C-22 polyunsaturated acids are common constituents of marine algal lipids, but no C-22 polyunsaturated acids have been detected in ferns.

It has been shown that in the leaf lipids of angiosperms [8] and conifers [4] there are wide variations in the proportions of certain polyunsaturated acids during the growing season. A study was made of the variations in the fatty acid compositions of the pinnae lipids of *P. aquilinum* and *D. filix-mas* from early May (fronds starting to unfurl) to the end of October (fronds withered), and of *P. vulgare* during the winter months. The variations in the proportions of certain of the polyunsaturated acids of *P. aquilinum* are shown in Fig. 1. It can be seen that there was a rapid increase in the early part of the season in the proportions of 18:3 ω-3 and (18:3 ω-3 + 16: ω-3) which reached maxima during August, after

Table 1. Fatty acid composition of total lipids of fern pinnae (% by weight)

Acid	*P. aquilinum* Range†	*P. aquilinum* Mean	*D. filix-mas* Range‡	*D. filix-mas* Mean	*P. vulgare* Range§	*P. vulgare* Mean	*D. austriaca*
12:0	tr–0·4	0·1	0·1–1·0	0·4	0·3–1·0	0·6	1·2
14:0	0·2–1·1	0·4	0·5–5·0	2·1	1·2–2·0	1·4	3·4
14:1	—	tr	—	tr	—	tr	tr
15:0	0·1–0·8	0·3	tr–0·3	0·1	0·3–0·6	0·4	0·5
16:0	15·6–26·8	19·9	14·0–23·4	19·6	14·5–15·8	15·0	17·0
16:1 ω-7 + 9	0·4–9·0	4·2	0·1–0·7	0·3	0·4–0·7	0·6	0·5
16:1 ω-13t	0·1–1·8	1·1	1·0–1·9	1·5	0·8–1·4	0·9	0·5
16:2 ω-6	0·1–0·7	0·4	0·1–0·9	0·3	0·5–0·8	0·7	0·2
16:3 ω-3	1·8–13·2	9·9	3·9–8·9	6·7	4·5–5·4	4·8	3·6
17:0	tr–0·4	0·1	0·1–0·2	0·1	—	0·2	0·4
18:0	1·0–4·1	2·0	1·1–1·8	1·3	0·4–0·7	0·6	1·3
18:1 ω-9*	3·0–8·5	5·0	2·9–9·0	5·2	4·8–10·5	6·9	4·2
18:2 ω-6	6·8–20·6	12·8	8·3–18·8	13·2	13·4–13·7	13·5	9·3
18:3 ω-6	tr–2·6	0·7	0·2–3·2	1·2	0·6–0·9	0·7	0·5
18:3 ω-3	13·2–42·0	30·9	20·2–40·0	34·4	30·6–39·8	34·9	45·4
18:4 ω-3	—	tr	tr–0·8	0·2	—	tr	0·6
20:0 } 20:1 }	0·5–2·6	1·4	1·0–3·0	2·1	2·0–3·5	2·9	1·8
20:2 ω-6	tr–0·5	0·1	0·1–0·8	0·2	0·1–0·2	0·2	0·2
20:3 ω-6	0·3–0·6	0·4	0·5–1·8	1·2	0·8–1·7	1·1	0·8
20:4 ω-6	4·5–12·8	7·3	4·3–10·2	6·8	9·1–11·1	10·0	5·6
20:4 ω-3	tr–0·2	tr	0·1–0·4	0·2	0·3–0·5	0·3	0·2
20:5 ω-3	0·3–4·0	1·5	1·3–2·5	1·9	2·1–2·8	2·2	2·1
22:0 } 22:1 }	0·3–3·2	1·5	0·5–1·3	1·0	1·9–3·4	2·1	0·7

tr—trace.
* Other isomers present.
† 9 Samples taken between May 1974 and October 1974.
‡ 6 Samples taken between May 1971 and October 1971.
§ 4 Samples taken between October 1971 and January 1972.

which there was a very rapid decrease. The proportion of 16:3 ω-3 reached a maximum some 8 weeks earlier and the subsequent decrease was not so rapid. The increase in proportions of the ω-3 acids was accompanied by a decrease in that of linoleic acid (18:2 ω-6) and the proportion of this acid reached a minimum at the time of the maxima for the ω-3 acids. During the first 6 weeks of the growing season there was a marked decrease in the proportions of 20:4 ω-6. The proportions of this acid did not then change much until the end of the growing season when there was a further slight decrease. Similar changes were found in the fatty acid composition of *D. filix-mas*. There was little change in the fatty acid composition of *P. vulgare* during the winter months.

The fatty acid compositions of several lipid classes from 3 fern species are shown in Table 2. It is found that the C-16 and C-18 polyunsaturated ω-3 acids are concentrated in the galactosyl diglycerides and account for 85·4–87·7% and 69·4–80·5% of the total acids of the monogalactosyl and digalactosyl diglycerides respectively. It is also found that 16:3 ω-3 is concentrated in the monogalactosyl diglycerides and appears to replace some of 18:3 ω-3 in this lipid class. This is similar to the distribution of 16:3 ω-3 in the galactosyl diglycerides of leaves of angiosperms, conifers and a moss. Only small amounts of 20:5 ω-3 were found in the digalactosyl diglycerides, but larger amounts were found in the monogalactosyl diglycerides and in the more polar lipid fractions (phospholipids, sulpholipids and some glycolipids). The ω-6 acids, linoleic and arachidonic, are also concentrated in the more polar lipids and are found in only small amounts of the galactosyl diglycerides. It might be expected that 16:2 ω-6 would also be concentrated in the more polar lipids, but the greatest proportions of this acid were found in the monogalactosyl diglycerides. Similar results were obtained by Auling *et al.* [9] for 16:2 ω-6 from a sample of *P. aquilinum*, and by Nichols [6] from a moss. In a recent investi-

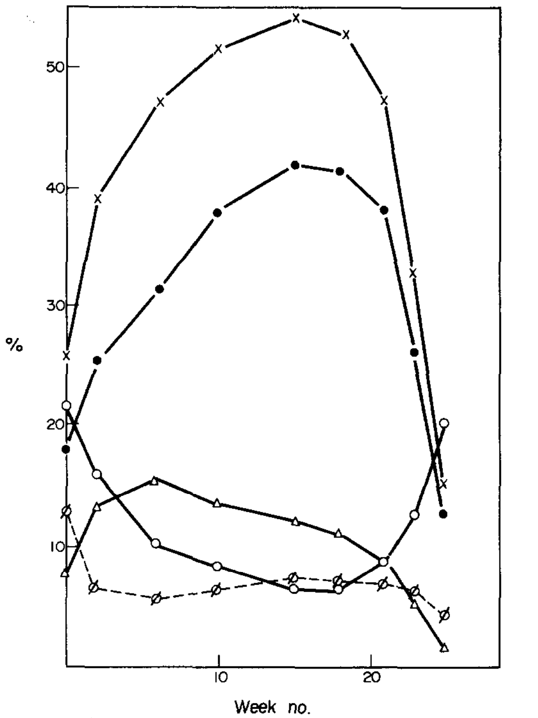

Fig. 1. ×—× 16:3 ω3 + 18:3 ω3; ●—● 18:3 ω3; △—△ 16:3 ω3; ○—○ 18:2 ω6; and ϕ---ϕ 20:4 ω6.

gation [10] of the sporophyte frond tissue of *P. vulgare* the reported fatty acid composition of the mono- and di-galactosyl diglycerides were similar to those found in the present work except for the total amounts of ω-3 acids. These investigators found 59 and 70% of ω-3 in the mono- and di-galactosyl diglycerides respectively (cf. Table 2). The unusual *trans*-acid, 16:1 ω-13t, was found only in the more polar lipids and in this respect fern lipids are similar to those of lipids from angiosperms, conifers and marine algae.

It has been shown [11] that, in a range of green plants, the ratio of the amounts of monogalactosyl (MGDG) to digalactosyl (DGDG) diglycerides varies widely (3·22–0·74). It has been suggested [11] that there may be a seasonal variation and has been shown [12] that there is a diurnal variation in this ratio. The ratio was determined for *P. aquilinum* during the growing season and the results are shown in Fig. 2. It was found that the MGDG/DGDG ratio increased slightly during the early part of the growing season, then remained fairly constant until the 16:3 ω-3 + 18:3 ω-3 reached the maximum value. There fol-

Table 2. Fatty acid composition of different lipid classes of fern pinnae (% by weight)

	12:0	14:0	14:1	15:0	16:0	16:1 ω-7 + 9	16:1 ω-13t	16:2 ω-6	16:3 ω-3	17:0	18:0	18:1 ω-9*	18:2 ω-6
D. filix-mas													
MGDG	tr	0·2	—	—	2·5	0·6	—	0·9	26·4	—	0·3	0·9	2·1
DGDG	0·2	0·3	—	—	16·0	0·6	—	0·3	3·9	—	0·7	4·6	4·7
More polar†	tr	0·5	tr	0·1	31·0	0·3	5·9	tr	tr	0·1	2·4	10·3	20·0
P. vulgare													
MGDG	tr	0·1	tr	0·1	3·4	0·6	—	1·4	20·8	—	0·2	1·0	2·1
DGDG	0·2	0·4	0·2	0·5	5·9	0·7	—	0·4	2·9	—	0·8	2·0	3·8
More polar	0·2	0·7	0·3	0·5	22·6	0·3	1·9	tr	tr	0·3	2·0	8·3	17·2
P. aquilinum													
MGDG	—	0·2	tr	tr	3·6	0·5	—	1·6	46·9	—	0·4	2·7	0·9
DGDG	tr	0·4	tr	0·3	5·1	1·5	—	0·4	4·6	—	1·8	11·4	6·1
More polar	tr	0·2	0·1	0·5	30·6	0·3	4·8	tr	0·9	0·1	2·0	15·1	18·3

	18:3 ω-6	18:3 ω-3	18:4 ω-3	20:0 20:1	20:2 ω-6	20:3 ω-6	20:4 ω-6	20:4 ω-3	20:5 ω-3	22:0 22:1	Total ω-3	Total ω-6
D. filix-mas												
MGDG	0·3	60·3	2·2	tr	tr	tr	1·0	0·2	2·1	tr	91·2	4·3
DGDG	0·5	66·6	tr	tr	tr	tr	1·1	0·1	0·2	0·2	70·8	6·6
More polar	2·6	8·0	tr	4·1	0·2	2·3	8·2	tr	1·8	2·2	9·8	33·3
P. vulgare												
MGDG	tr	63·4	0·2	tr	tr	0·1	0·4	0·4	4·8	tr	90·6	4·0
DGDG	tr	77·6	tr	tr	tr	1·0	1·7	0·1	0·9	0·9	81·5	6·9
More polar	0·6	19·0	tr	3·2	0·4	1·5	17·4	tr	2·2	1·4	21·2	37·1
P. aquilinum												
MGDG	0·1	40·0	0·8	tr	tr	0·2	1·3	0·2	0·6	tr	88·5	4·1
DGDG	0·3	64·8	tr	tr	tr	0·8	2·0	0·1	tr	0·4	69·5	9·6
More polar	0·6	10·1	tr	2·8	0·5	1·2	9·7	tr	0·9	1·3	11·9	30·3

* Other isomers present: tr—trace.

† Phospholipids, sulpholipid and unidentified glycolipids.

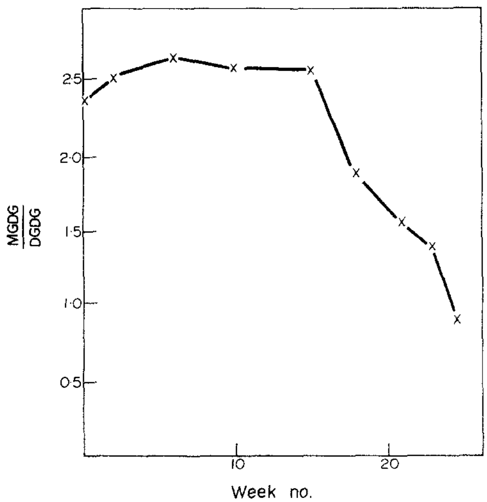

Fig. 2.

lowed a rapid fall in the MGDG/DGDG ratio indicating a decrease in the relative proportion of MGDG.

EXPERIMENTAL

Samples of ferns were collected in the surrounding districts of Paisley. *P. aquilinum* samples were collected from the same location at Rowbank Reservoir at 13·30 hr. Lipids were extracted and separated into classes by methods described previously [1–5]. GLC analysis of the total lipid methyl esters and the methyl esters from each of the lipid classes were carried out on a PE 800 chromatograph using open tubular columns of different polarity [13]. MGDG and DGDG were determined by GLC of the trimethylsilyl derivatives of the glycosyl glycerols obtained by deacylation of the total lipids [14]. GLC of these derivatives was carried out on a PE F11 chromatograph with the following operating conditions: 3% OV-1 Chromosorb WAW-DMCS 80–100 mesh. 40 cm × $\frac{1}{8}$ in. stainless steel (Phasesep Ltd.); temperature programmed 180–280°. 5° per min.

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