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THE OCCURRENCE OF HEXADECA-7,10,13-TRIENOIC ACID IN THE LEAF LIPIDS OF ANGIOSPERMS

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Abstract—Hexadeca-7,10,13-trienoic acid, a lower homologue of linolenic acid, is found in the leaf lipids of a variety of angiosperm species. The acid is found to be concentrated in the monogalactosyl diglyceride and diglyceride fractions of the leaf lipids.

INTRODUCTION

THE MAJOR constituent fatty acids of the leaf lipids of higher plants are palmitic, linoleic and linolenic acid; the proportion of linolenic acid (18:3ω3) in most species being greater than 40% of the total acids. The presence of hexadeca-7,10,13-trienoic acid (16:3ω3), a lower homologue of linolenic acid, has been reported in the leaf lipids of a few angiosperm species.[1–5]

It has been found that monogalactosyl diglyceride (MGDG) and digalactosyl diglycerides (DGDG), the major constituents of the chloroplast lipids of higher plants, have a high linolenic acid content.[6] This acid is thought to be necessary for the photosynthetic production of oxygen.[7] The galactolipids from wheat flour, a non-photosynthetic tissue, have been found to contain little linolenic acid.[8] It has been shown[4] that, in spinach, both 18:3ω3 and 16:3ω3 are concentrated in the galactolipids and also that 16:3ω3 is preferentially concentrated in the MGDG fraction.

During a survey of the leaf lipids of higher plants it was found that 16:3ω3 was more widely distributed among different species than is indicated in the literature and it is of interest to examine the distribution of this acid among the different lipid classes.

RESULTS AND DISCUSSION

During the last few years we have been carrying out a survey of the fatty acid composition of the leaf lipids of green plants and some of these compositions have been published.[9–11] Linolenic acid was found to be the most abundant acid present in all the species studied. The lower homologue of linolenic acid, 16:3ω3, was found to be present in many species

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and the proportions of this acid in the different species examined are shown in Table 1 and the distribution of the amounts of 16:3ω3 among the different species in Table 2. It was found that when 16:3ω3 was present in one member of a family it was present in similar amounts in the other members of the family. In some families there were greater variations in the amounts of 16:3ω3 among the members but it has been shown[10] that there is a variation in the proportions of fatty acids during the growing cycle of higher plants.

Table 1. Amounts of 16:3ω3 in the total lipids of Angiosperm leaves

Species		% 16:3ω3
ROSALES		
Rosaceae		
Sorbus aucuparia	Rowan	3 5
Alchemilla vulgaris	Lady's Mantle	0·9
Geum rivale	Water Avens	1·2
Rubus idaeus	Raspberry	0·1
Potentilla palutris	Marsh Cinquefoil	1·0
CUNONIALES		
Grossulariaceae		
Ribes sanguineum	Flowering Currant	12 6
R. uva-crispus	Gooseberry	7·9
ARALIALES		
Araliaceae		
Hedera helix	Ivy	6·2
Caprifoliaceae		
Lonicera periclymenum	Honeysuckle	3·8
Sambucus nigra	Elder	5·5
FAGALES		
Betulaceae		
Betula pendula	Silver Birch	1·8
Fagaceae		
Quercus robur	Oak	tr
Fagus sylvatica	Beech	tr
URTICALES		
Ulmaceae		
Ulmus procera	Elm	0·2
SAPINDALES		
Aceraceae		
Acer pseudoplantanus	Sycamore	0·5
A. campestre	Maple	0·1
Hippocastanaceae		
Aesculus hippocastanum	Horse Chestnut	2·1
RUBIALES		
Rubiaceae		
Gallium odoratum	Sweet Woodruff	9·1
G. aparine	Goose Grass	11·0
RANALES		
Ranunculaceae		
Aquilegia vulgaris	Columbine	9·8
Caltha palustris	March Marigold	10·8
Ranunclus acirs	Meadow Buttercup	17·5
R. ficaria	Lesser Celandine	13·9
Anemone nemerosa	Wood Anemone	15·1
Delphinium ambiguum	Larkspur	17·4
BERBERIDALES		
Berberidaceae		
Berberis vulgaris	Barberry	4·1

TABLE 1 (*cont.*)

Species		% 16:3ω3
CRUCIALES		
Brassicaceae		
Cardamine pratensis	Lady's Smock	11·3
Cheiranthus cheiri	Wallflower	11·1
Nasturtium officinale	Watercress	16·9
Brassica oleacea	Cabbage	15·9
CARYOPHYLLALES		
Caryophyllaceae		
Stellaria graminea	Lesser Stitchwort	0·5
S. holstea	Greater Stitchwort	0·2
S. alsine	Bog Stitchwort	0·1
S. media	Chickweed	0·1
Silene dioica	Red Campion	0·3
S. alba	White Campion	0·2
S. vulgari	Bladder Campion	0·1
Lychnis coronaria	Rose Campion	0·4
L. flos-cuculi	Ragged Robin	0·2
Gerastium glomeratum	Mouse-Eared Chickweed	tr
Portulaceae		
Montia perfoliata		11·5
CHENOPODIALES		
Chenopodiaceae		
Spinacia oleracea	Spinach	11·8
ONAGRALES		
Onagraceae		
Chamaenerion augustifolium	Fireweed	0·4
Ephilobium montanum	Broad Leafed Willow Herb	0·6
Circaea lutetiana	Enchanter's Nightshade	0·6
Callitrichaceae		
Callitriche stagnalis		tr
PRIMULALES		
Primulaceae		
Lysimachia vulgaris	Yellow Loosestrife	tr
Plumbaginaceae		
Armeria maritima	Thrift	0·5
PLANTAGINALES		
Plantaginaceae		
Plantago major		tr
P. lanceolata		0·1
SAXIFRAGALES		
Crassulaceae		
Sedum rosea	Roseroot	0·1
S. acre	Wall Pepper	0·1
S. fabaria		0·1
Saxifragaceae		
Philadelphus sp.	Hydrangea	tr
Saxifraga umbrosa	London Pride	tr
UMBELLALES		
Apiaceae		
Chaerophyllum temulentum	Chevril	16·2
Daucus carota	Wild Carrot	16·7
Heracleum sphondilium	Hogweed	16·6
VALERIANALES		
Valeraniaceae		
Valeriano officinalis	Valerian	9·7

TABLE 1 (*cont.*)

Species		% 16:3ω3
CAMPANELES		
Campanulaceae		
Jascone montana	Sheepsbit	12·2
Campanula rotundifolia	Harebell	8·4
SOLANALES		
Solanaceae		
Solanum tuberosum	Potato	11·6
S. dulcamara	Woody Nightshade	9·6
Lycopersicum esculentum	Tomato	13·8
Convolvulaceae		
Calystegia sepium	Bindweed	tr
GERANIALES		
Geraniaceae		
Erodium dunense	Dune Storksbill	8·7
Geranium robertianum	Herb Robert	8 3
LAMINALES		
Laminaceae		
Ajuga reptans	Bugle	0·2
Lamium molecellifolium	Intermediate Dead Nettle	0 2
LILIALES		
Liliaceae		
Convallria majalis	Lily of the Valley	0·6
Polygonatum multiflorum	Solomon's Seal	2·0
IRIDALES		
Iridaceae		
Iris pseudacorus	Yellow Flag	1·8
ORCHIDALES		
Orchidaceae		
Orchis latifola		0·3
JUNCALES		
Juncaceae		
Juncus conglomeratum	Common Rush	0·2

Species in which 16:3ω3 was not detected

LEGUMINALES	
Fabaceae	
Sarothamnus scoparis	Broom
Ulex europus	Gorse
URTICALES	
Urticaceae	
Urtica dioica	Stinging Nettle
VIOLALES	
Violaceae	
Viola riviniana	Common Violet
V. wiltrockiana	Pansy
ERICALES	
Ericaceae	
Rhododendron ponticum	Rhododendron
Vaccinium myrtillus	Bilberry
Erica cinerea	Heather
GUTTERIFERALES	
Hypericaceae	
Hypericum tetrapterum	Square Stalked St. John's Wort
H. androsaemum	Tutsen

TABLE 1 (*cont.*)

Species in which 16:3ω3 was not detected	
LOGANIALES	
Oleaceae	
Ligustrum vulgaris	Privet
S. vulgaris	Lilac
RANALES	
Nymphaceae	
Nuphar lutea	Yellow Water Lily
RHOEDALES	
Papveraceae	
Papaver rhoeas	Poppy
Meinopsis cambrium	Welsh Poppy
Fumariaceae	
Fumaria officinalis	Fumıtory
POLYGONALES	
Polygonaceae	
Rumex obtusifolius	Broad Leafed Dock
Polygonum amphibium	Amphibious Persicaria
GENTIALES	
Gentianaceae	
Menyanthus trifoliata	Bogbean
ASTERALES	
Asteraceae	
Centaura nigra	Knapweed
Taraxacum officinale	Dandelion
Senecio jacobaea	Ragwort
Achillea millefolium	Yarrow
Onaporun acanthium	Scottish Thistle
PERSONALES	
Scrophulariaceae	
Linaria vulgaris	Common Toadflax
Veronica chaemaedris	Germander Speedwell
Antirrhinum majus	Snapdragon
GERANIALES	
Oxalidaceae	
Oxalis acetosella	Wood Sorrel
BORAGINALES	
Boraginaceae	
Myosotis scorpioides	Water Forget-me-not
M. arvensis	Common Forget-me-not
M. alpestris	Alpine Forget-me-not
Cynoglossum amabile	
Symphytum officinale	Comfrey
Echium vulgare	Viper's Bugloss
Pulmonaria officinalis	Lung Wort
Mertensia maritima	Northern Shorewort
LILIALES	
Amaryllidaceae	
Galanthus rivalis	Snowdrop

TABLE 2. DISTRIBUTION OF 16:3ω3 IN ANGIOSPERM SPECIES

%16:3ω3	Not detected	tr–1%	2–5%	6–10%	11–20%
No. of species	37	36	8	10	19
		Total 73			

TABLE 3. FATTY ACID COMPOSITION OF DIFFERENT LIPID CLASSES OF ANGIOSPERM LEAVES

	% By weight									
	16:0	16:1 ω7+9	16:1 ω13t	16:2 ω6	16:3 ω3	18:0	18:1	18:2 ω6	18:3 ω3	Total ω3
Ribes sanguineum										
TG	17·9	0·2	—	tr	2·9	9·4	15·0	14·5	40·1	43·1
DG	35·2	0·4	—	tr	14·7	2·9	9·1	6·5	31·2	45 9
MGDG	3·2	1·1	—	0·1	23·2	0·3	0·7	1·9	69·5	92·7
DGDG	6·4	1·5	—	0·3	6·8	0·6	0·2	3·2	81·0	87 8
Polar	18·3	0·7	6·2	0·1	0·1	0·4	1·3	18·1	54·8	54 9
Hedera helix										
TG	7·8	0·2	—	0·3	1 9	3·2	7 9	51·9	26·8	28·7
DG	21·6	0·4	—	0·2	8 9	2·0	4·5	28·2	34·2	43 1
MGDG	2 2	0 2	—	2·6	35·6	0·3	0·6	5·3	53 2	88·8
DGDG	9 0	0·1	—	0·3	1·6	0·8	1 0	13 8	73 4	75·0
Polar	19·6	tr	1·4	0·4	1 1	1·0	3 6	56·5	16·4	17 5
Sambucus nigra										
TG	38·2	tr	—	tr	3·9	14·5	15·5	9·4	18·5	22·4
DG	59·1	tr	—	tr	10 2	5·7	3·7	3 7	17·6	27·8
MGDG	2·7	tr	—	0·1	5·1	0 2	0·3	1·1	90 5	95·6
DGDG	5·6	0·1	—	0·1	2·5	0 7	0·2	1·0	89 8	92·3
Polar	25·1	0·2	4·4	tr	0·2	2·5	1·0	27·6	39 0	39·2
Galium odoratum										
TG	12·4	0 5	—	tr	1·2	7·2	16·4	24·6	37·7	38·9
DG	42·6	0·6	—	tr	12·7	5·1	3·6	8·1	27·3	40·0
MGDG	1·8	0·3	—	0·4	34·7	0·2	0 4	1·5	60·7	95·4
DGDG	7·7	0·2	—	0 1	8·6	0·7	1·1	6 7	74·9	83·5
Polar	22·7	0·1	4·6	0·1	0·4	1·6	2 9	21 8	45·8	46·2
Ranunculus acris										
TG	11·5	1·1	—	tr	1·0	5·3	14·8	35·4	30 9	31·9
DG	34·3	0·7	—	tr	9·6	5·0	4·1	8·0	38·3	47·9
MGDG	1·3	0·3	—	1 6	36·8	0·4	0·5	1·1	58·0	94 8
DGDG	6·3	0·1	—	0·3	3·5	0·4	0·3	1·5	87·6	91·1
Polar	19·7	0·3	6 4	0·2	0 4	1·2	1·8	17 0	53·0	53·4
Montia perfoliata										
TG	14·6	tr	—	tr	2·1	6·4	8·6	15·6	52 7	54·8
DG	38·7	tr	—	tr	15·2	2 7	1·6	7·2	34·6	49·8
MGDG	1·1	0·3	—	0·5	19 6	0·3	0 4	1·3	76·5	96·1
DGDG	7·5	0·5	—	1·0	4·5	0·8	1·4	2·4	81·9	86·4
Polar	18·0	tr	5·1	3·2	1·9	0·7	3·0	20·9	47·2	49·1
Heracleum sphondylium										
TG	18·6	tr	—	0·1	1·8	5·6	14 9	39·2	19·8	21·6
DG	41·9	tr	—	0·2	28·4	3·7	2·9	7·6	15·3	43·7
MGDG	1·0	0·2	—	0·7	55·3	0 4	0·6	0·7	41·1	96·4
DGDG	10·8	0·1	—	0·3	7·5	0 5	0·6	4·9	75·3	82·8
Polar	18 9	0 1	7·6	tr	2·6	0·6	0·9	42·8	26·5	29·1
Lycopersicon esculentum										
TG	15·1	tr	—	0·1	1·6	6·2	10·4	29 6	37·0	38·6
DG	44·6	0·1	—	0·2	22·7	1·8	1 6	6·8	22·2	44·9
MGDG	2·4	0·3	—	0·7	32·4	0·3	0·6	4·4	58 9	91·3
DGDG	9·8	0·2	—	0·2	3·3	1·6	2·4	7 1	75·4	78·7
Polar	21·8	0·5	3·4	0·1	1·5	1·8	4·1	34·0	32·8	34·3
Spinacia oleracea										
TG	16 7	tr	—	tr	1·2	4·8	12·6	22·2	42·5	43·7
DG	42·7	0·1	—	0·1	26·8	1·2	1·4	8·2	19·5	46·3
MGDG	1·5	0·3	—	0·1	21·9	0·3	0 8	1·6	73·5	95·4
DGDG	7·6	0·1	—	tr	6·9	0·9	1·6	5·6	77·3	84·2
Polar	19·2	0·2	2·9	tr	1 0	1·0	2·4	31·7	41·6	42·6
Iris pseudacorus										
TG	18·2	tr	—	tr	0·5	5·7	15·2	32·4	28 0	28·3
DG	39·8	0·1	—	0·2	8·9	1·2	2·2	7·5	40·1	49 0
MGDG	0·8	0·4	—	0·3	9·7	0·2	0·6	1 4	86·6	96·3
DGDG	8·2	0·3	—	tr	0 7	0·8	1·4	6·2	82·4	83·1
Polar	32·4	0·3	2·4	tr	0·1	1·2	3·7	35·6	24·3	24·4

The fatty acid composition of different lipid classes of ten species are shown in Table 3. It is found that the ω3 acids are concentrated in the galactosyl diglycerides accounting for 88·8–96·4% and 75·0–86·4% of the total acids of the monogalactosyl and digalactosyl diglycerides respectively. These findings are similar to those already reported for the fatty acid compositions of the galactolipids of *Myosotis scorpioides*[9] and *Stellaria media*[11] where the main ω3 acids are 18:3ω3 and 18:4ω3.

It is also found that in each of the species studied that there is a preferential concentration of 16:3ω3 in the monogalactosyl diglycerides. The digalactosyl diglycerides have relatively small amounts of 16:3ω3 but, in general, have greater amounts of 18:3ω3 than the monogalactosyl diglycerides. It would thus appear that, in the monogalactosyl diglycerides, 18:3ω3 is replaced, in part, by the lower homologue 16:3ω3.

There are conflicting opinions concerning the biosynthetic pathways leading to the formation of galactosyl diglycerides in plants.[12–15] In a recent report by Mudd *et al.*[16] it was suggested that the first galactosylation was a reaction specific for a highly unsaturated diglycerice acceptor and they also found that the greatest stimulation of galactolipid synthesis by diglycerides from spinach leaf phospholipids was by the more highly unsaturated species. They also suggested that the synthesis of these galactolipids may be achieved by a selective utilization of unsaturated diglycerides from a pool of diglycerides of various degrees of unsaturation. The results in Table 3 show that the diglyceride fractions contain relatively high proportions of 16:3ω3 and could constitute the pool of diglycerides, postulated by Mudd, from which the galactopilids are synthesized.

EXPERIMENTAL

Plants were collected from various areas in the surrounding districts of Paisley, and lipids were extracted and separated into classes by methods described previously.[9,10]

GLC analyses of the total lipid methyl esters and the methyl esters from each of the lipid classes were carried out on a PE800 chromatograph employing various polyester open tubular columns.[17]

Plant species were identified using methods described by Clapham *et al.*[18] and identifications verified by the Biology Dept., The Paisley College of Technology. Orders were arranged according to Hutchison.[19]

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