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THE COMPONENT FATTY ACIDS OF SOME MARINE ALGAL LIPIDS

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Abstract—Twelve marine algae of the Rhodophyta, 17 of the Phaeophyta and 5 of the Chlorophyta were analysed for their fatty acid content. It is possible that the fatty acid distribution may be useful for taxonomic purposes. It is found, that, as in higher plants, there are specific fatty acid distributions in the galactosyl diglycerides, e.g. the ω3 acids with the highest unsaturation are concentrated in the monogalactosyl diglycerides.

INTRODUCTION

ALTHOUGH a number of investigations have been carried out on the fatty acid compositions of marine phytoplankton lipids,[1,2] very little is known about the component fatty acids of seaweeds. In the present investigation 34 species of marine algae of different phyla were analysed and a comparison made of the component fatty acids to assess the usefulness of fatty acid distribution for taxonomic purposes. The data obtained suggest that the fatty acids present in seaweeds are similar to those present in fish oils although there are quantitative differences. In seaweeds and fish oils the highly unsaturated C_{16}, C_{18} and C_{20} acids predominate, but in seaweeds C_{22} polyunsaturated acids are present in only minor amounts whereas in fish oils these acids are major components.

It has been found that the galactosyl diglycerides of higher plants have specific fatty acid compositions[3–6] and an investigation was carried out on some of the marine algal species to see if there was a specific distribution of the polyunsaturated acids in the mono- and digalactosyl diglycerides and to compare the distributions with those obtained in higher plants.

RESULTS

Rhodophyta

The twelve Rhodophyta species studied all show characteristically similar fatty acid distributions (Table 1). The major constituent fatty acids of each species are 16:0 and 20:5ω3. The only other C_{20} polyunsaturated acid present in significant amounts is 20:4ω6 Various C_{18} polyunsaturated acids are present in each species but only in a few cases is the amount of any particular acid greater than 5%. A number of C_{16} polyunsaturated acids are present usually in amounts less than 2%.

Our results for *Rhodomela subfusca* and *Ceramium rubrum* are similar to those published by Klenk, *et al.*[7] although these workers found higher proportions of 16:0 than in the present

[1] R. G. ACKMAN, C. S. TOCHER and J. MCLACHLAN, *J. Fish. Res. Bd. Canada* **25**, 1603 (1968).
[2] L. CHEUCAS and J. P. RILEY, *J. Mar. Biol. Ass. U.K.* **49**, 97 (1969).
[3] G. R. JAMIESON and E. H. REID, *Phytochem.* **8**, 1489 (1969).
[4] G. R. JAMIESON and E. H. REID, *Phytochem.* **10**, 1575 (1971).
[5] G. R. JAMIESON and E. H. REID, *Phytochem.* **10**, 1837 (1971).
[6] G. R. JAMIESON and E. H. REID, *Phytochem.* **11**, 269 (1972).
[7] E. KLENK, W. KNIPPRATH, D. EBERHAGEN and H. P. KOOF, *Z. Physiol. Chim.* **334**, 44 (1963).

TABLE 1. FATTY ACID COMPOSITION

		% by weight										
		12.0	14:0	14·1	16·0	16·1 ω7+9	16:1 ω13t	16 2 ω6+4	16 3 ω6+4	16:3 ω3	16 4 ω3	18:0
Dumontia crispata	Mar. 70	0 1	2·2	tr.	17·0	6·0	1 0	0 5	0 1	0 3	0 6	0 3
Schizymenia dubyi	Aug. 70	0 1	1 4	tr.	22 0	2 0	0 9	tr.	0 2	0 1	0 4	0·5
Corallina officinalis	Feb. 71	0·1	1·7	0 1	23 5	2 8	0 5	0 8	0 5	0 5	0 8	1·1
Cryptopleura ramosum	Mar. 70	0·2	7 1	0 1	19·9	1 5	1 1	0 1	tr	tr	1 0	0·2
Rhodomela subfusca	Feb. 70	0 1	2 3	0 2	17 8	5 8	2 7	1 6	0 3	0·6	1·0	1·3
	Feb. 71	0 1	1 3	0 3	18 1	0 3	0 6	2 6	0 2	0 5	1 2	0 3
Odonthalia dentata	May 70	0 1	3 0	0 1	26 6	1 6	0 7	0 2	tr.	0 2	0 1	1 1
Laurencia obtusa	Mar. 70	0 1	1 5	0 1	18 0	5 2	1 8	0 3	0 5	0 6	1 8	0 2
	Feb. 71	0 1	3 8	0 3	23 0	0 9	0 5	1 2	0 7	0 7	0 5	1 2
L. pinnatifida	Jan. 70	0 3	4 3	0 3	20·9	3 0	1 0	0 3	0 5	0 5	0 9	3 7
Ceramium rubrum	Jul. 68	0 1	2 9	0 4	23·3	5 0	0 7	0 2	0 4	tr.	0 4	1 2
	Dec. 68	0 2	2 9	0 4	21·0	6·0	1 8	5 7	1 9	tr.	1·9	1 5
Chondrus crispus	Jan. 70	0 2	2 1	0 1	17·6	3 8	0 8	2 4	1 0	tr.	3 3	1 0
Gigartina stellata	Jun. 70	0 1	3 4	0 2	20 0	2 5	1·2	0 2	0 2	0·2	0 5	2·3
Chylocladia kaliformis	Mar. 70	0 3	4 3	0 2	22 3	3 1	0 7	0 6	0 5	0 3	0 3	0 3

tr.—trace.

* Other isomers present.

work. Pohl *et al.*[8] analysed four Rhodophyta species but did not report the presence of 16:3, 16:4, 20:3 and C_{22} polyunsaturated acids and only moderate amounts of 20:4ω6 and 20:5ω3. They did not find any 18:3ω3 or 18:4ω3 in a sample of *Laurencia obtusa*. Cheucas and Riley[9] did not report the presence of 18:3ω3, 18:4ω3, C_{16} and C_{22} polyunsaturated acids in samples of *Rhodomenia palmata* and *Laurencia pinnatifida* and only found 20:5ω3, in the latter species.

The fatty acid compositions of different lipid classes of three species are given in Table 2. The highest concentrations of the C_{16}, C_{18} and C_{20}, acids with the highest unsaturation, viz. 16:4ω3, 18:4ω3 and 20:5ω3, are found in the monogalactosyl diglycerides. The highest proportions of 16:3ω3 are found in the digalactosyl diglycerides and those of 20:4ω6 in the polar lipids.

TABLE 2. FATTY ACID COMPOSITION OF

	% by weight										
	14:0	14:1	16:0	16:1 ω7+9	16:1 ω13t	16:2 ω6+4	16:3 ω6	16:3 ω4+3	16:4 ω3	18:0	18:1 ω9*
Corallina officinalis											
MGDG	0·6	0·2	9·4	0·5	—	0·7	0·8	3·9	4·7	0·3	2·3
DGDG	1·0	0·3	24·9	0·6	—	0·3	1·2	4·6	0·5	0·7	3·5
Polar	2·5	0·3	27·7	1·9	1·5	0·1	0·6	1·0	0·1	0·3	3·2
Ceramium rubrum											
MGDG	1·5	0·2	13·2	3·7	—	10·8	0·1	2·3	4·3	0·2	5·4
DGDG	2·3	0·2	29·5	7·1	—	5·2	0·3	4·0	1·2	0·5	7·4
Polar	2·7	0·2	24·6	3·0	2·1	3·5	tr.	2·6	0·2	3·0	19·0
Chondrus crispus											
MGDG	1·9	0·2	12·8	1·9	—	3·6	tr.	1·8	7·6	1·6	7·2
DGDG	4·0	0·2	24·0	3·8	—	4·0	tr.	2·0	2·9	1·9	9·8
Polar	3·0	0·1	24·2	3·8	2·1	0 9	tr.	0·5	tr.	1·3	14·4

tr.—trace; MGDG—monogalactosyl diglycerides; DGDG—digalactosyl diglycerides; Polar—more polar lipids.

* Other isomers present.

[8] P. POHL, H. WAGNER and T. PASSIG, *Phytochem.* **7**, 1565 (1966).

[9] L. CHEUCAS and J. P. RILEY, *J. Mar. Biol. Ass. U.K.* **46**, 153 (1966).

OF TOTAL LIPIDS OF RHODOPHYTA

% by weight														
18:1 ω9*	18:2 ω6	18:3 ω6	18:3 ω3	18:4 ω3	20:0 20:1	20:2 ω6	20:3 ω6	20:4 ω6	20:4 ω3	20:5 ω3	22.0 22:1	22:4 ω6	22:5 ω3	22:6 ω3	24.0 24:1
4·4	1·9	0·5	3·3	6·5	0·2	0·1	0·3	2·5	0·4	51·3	0·2	tr.	0·3	tr.	tr.
4·6	1·9	0·6	2·6	3·0	1·3	0·3	0·3	7·5	0·4	49·8	0·1	tr.	tr.	tr.	tr.
4·6	2·2	0·5	0·6	0·8	0·4	0·2	0·5	5·5	0·4	51·6	0·2	tr.	0·3	tr	tr.
4·0	1·9	0·3	1·5	2·5	0·2	0·1	0·8	3·8	0·4	50·9	0·2	tr.	1·5	0·5	0·2
11·1	4·3	0·3	1·7	2·0	0·6	0·4	0·5	9·1	0·1	35·8	0·2	tr.	0·1	tr.	0·1
5·0	2·6	0·5	2·1	3·0	0·7	0·3	0·4	9·9	0·3	43·6	0·7	0·3	1·6	1·1	0·9
11·3	1·0	0·7	0·3	0·3	0·1	0·2	1·0	13·2	0·1	37·8	0·4	tr.	tr.	tr.	tr.
4·7	2·0	0·5	2·7	3·0	0·8	0·4	0·4	9·0	0·6	42·5	0·9	0·2	0·4	0·9	0·4
5·3	2·3	0·5	1·8	2·1	0·3	0·2	0·4	4·5	0·1	47·6	0·5	0·6	0·3	0·4	0·3
7·9	4·9	0·5	0·3	3·5	0·3	0·4	0·5	6·3	0·4	35·4	0·3	0·1	0·4	tr.	0·1
11·1	4·2	0·5	2·5	2·0	0·3	0·3	1·0	9·1	1·0	32·4	0·3	tr	0·5	tr.	0·2
10·4	3·0	0·5	3·3	3·7	0·4	0·3	0·4	8·3	0·4	25·6	0·2	0·1	0·1	tr.	0·1
11·2	3·5	0·5	5·8	5·6	0·4	0·4	0·7	12·5	0·4	26·4	0·2	tr.	0·1	tr.	0·1
12·5	2·9	0·7	2·9	2·7	0·4	0·2	0·5	17·7	0·3	27·6	0·3	tr.	0·2	0·1	0·2
6·0	0·8	0·3	0·2	0·7	0·2	0·3	0·2	5·7	tr.	49·1	0·2	0·4	2·0	0·6	0·4

Phaeophyta

The fatty acid compositions of sixteen Phaeophyta species are shown in Table 3. Generally the species have higher proportions of C_{18} polyolefinic and small proportions of C_{20} polyolefinic acids than the Rhodophyta species. In the majority of Phaeophyta species the proportion of 20:4ω6 is higher than that of 20:5ω3, the major constituent fatty acid of the Rhodophyta. Only very small proportions of any C_{16} polyolefinic acid are present in the Phaeophyta species studied. High proportions of 18:1 were found in *Ascophyllum nodosum*, *Pelvetia canaliculata* and in some of the *Fucus* samples. An interesting feature is the presence of a C_{20} non-methylene-interrupted polyolefinic acid, 20:3,^{5,11,14} in certain of the species; the concentration of this acid reaching 3·6% in *A. nodosum*. Although the presence of this type of acid is unusual in plant species, 20:3,^{5,11,14} and similar Δ^5 acids have recently been reported in conifers[6] and Equisetales.[10]

DIFFERENT LIPID CLASSES OF RHODOPHYTA

% by weight												
18:2 ω6	18:3 ω6	18:3 ω3	18:4 ω3	20:0 20:1	20:2 ω6	20:3 ω6	20:4 ω6	20:4 ω3	20:5 ω3	22:0 22:1	Total ω3	Total ω6
1·7	0·5	3·4	8·6	0·2	0·1	0·1	4·4	0·4	57·2	tr.	78·2	8·3
1·3	0·6	3·6	4·4	1·2	0·2	0·3	4·5	0·2	45·9	0·2	60·2	8·4
1·3	0·7	3·2	2·1	1·5	0·3	0·4	8·2	0·2	42·5	0·4	49·1	11·6
2·5	0·3	4·5	4·6	0·3	0·1	0·5	6·5	0·6	38·4	tr.	54·7	20·8
4·8	0·3	3·0	1·9	0·3	0·1	1·2	4·2	0·3	26·2	tr.	36·6	16·1
3·6	0·4	3·0	0·7	0·5	0·5	0·6	9·8	0·3	19·1	0·6	25·9	18·4
2·4	0·4	12·6	11·4	0·2	0·5	0·3	5·9	0·2	27·5	tr.	61·3	13·1
2·8	0·2	6·8	5·4	0·3	0·7	0·6	7·2	0·3	23·0	0·1	40·4	15·5
3·4	0·4	5·4	1·9	0·4	0·7	0·2	15·0	0·2	21·5	0·6	30·5	20·6

[10] H. SCHLENK and J. L. GELLERMAN, *J. Am. Oil Chem. Soc.* **42**, 504 (1965).

TABLE 3. FATTY ACID COMPOSITION

		% by weight										
		12:0	14:0	14:1	16:0	16:1 ω7+9	16:1 ω13t	16:2 ω6+4	16:3 ω6,4,3	16:4 ω3	18:0	18:1 ω9*
Ectocarpus confervoides	Mar. 70	tr.	2·4	0 2	11·0	1 5	1·5	0·2	0 3	0 4	0 4	5 9
Leathesia difformis	Jun. 70	0 2	5 4	tr.	23·2	2 0	1·0	0 3	0 5	tr.	1·3	10 8
	Jun. 71	0·5	4 6	tr.	19·2	0 9	0 8	0 6	1 8	0 6	1·7	8·9
Chordaria flagelliformis	Aug. 70	0 2	5 8	tr.	17·8	0·4	1 0	0 2	0 1	0·2	2·1	15 2
Desmarestia aculeata	Jul. 68	tr.	5 7	0 4	20 9	3·0	2 8	0 9	1·0	0·2	0·4	11·2
	Apr. 70	0 1	4·1	tr.	12·3	1 1	1·0	0 4	0 3	0 2	0·4	6 9
Dictyosiphon foeniculaceus	Apr. 70	0 1	4·5	0 3	12 4	2 0	2·7	1 1	0 2	0 7	1 2	7 2
Punctaria plantaginea	May 70	tr.	3 6	0 1	16 2	0·9	0 3	0 1	0 1	0·1	1·1	13·5
Chorda Filum	Jul. 71	tr.	3·5	0 1	27·6	0·7	0·7	tr.	0 1	0·1	1·2	17·8
Laminaria saccharina	Jan. 70	tr.	4 0	0 1	10 2	2 1	0 9	0·1	0·1	0·1	0 3	8·1
L. digitata	May 70	tr.	4 0	0 1	11 9	1·1	0 8	tr.	0 1	tr.	0·4	12·7
Alaria esculenta	Feb. 70	tr.	4 8	0·2	10 1	1·5	0 9	0·1	0·1	0·1	0 5	6 5
Fucus spiralis	Jun. 68	0 2	12·4	0·1	16 3	1 4	0·5	0·5	0 1	tr.	0 5	19 3
	Nov. 69	0 2	10·8	0 5	12 8	2·0	0·5	0 2	0·3	0 4	0·9	14·6
	Jun. 70	0·1	9·1	0 1	9·4	1·0	0·3	0·3	0 4	0 4	1·1	38·2
F. Vesiculosus	Apr. 70	0·1	3·8	0·1	11·2	1·0	0·2	0·3	0·3	0·7	0·2	17·1
F. Vesiculosus var. *evesiculosus*	Dec 70	0 1	10·0	0 2	12·4	1 8	0 4	0·1	0·3	0·5	0·3	12 4
F. serratus	Jun. 68	0 1	11·7	0 1	15·6	1·4	0 3	0·5	0·1	tr.	0·4	27 4
	Nov 69	0 1	7 3	0 4	14·4	2 0	0 8	0 5	0 1	1 3	0·8	14·9
Ascophyllum nodosum	Jun. 68	0·1	7·1	0·2	11 0	1 7	0·6	0 5	0 4	0·3	0 4	34·4
	Nov. 70	0·2	7 4	0 2	9·8	1·5	0 3	0 2	0·3	0·1	0·8	30·4
Pelvetia canaliculata	Jun. 68	0·1	7·0	0 1	10·2	1·0	0 5	tr.	tr.	tr.	1·2	29·9
	Jun. 70	0 1	6 8	0·1	9·3	1·3	0·1	0 3	0 3	0 4	2 2	38 8
	Aug. 70	tr.	6 5	0 1	10 2	1·3	0·1	0·2	0·2	0·3	1·9	37 4
Halydris siliquosa	Feb. 70	0 1	7 8	tr.	14 6	0·9	0·2	0 2	0 2	0·2	0·5	12·0

tr.—trace.
* Other isomers present.

Klenk *et al.* have reported[7] the fatty acid compositions of three *Fucus* species and their results are similar to those in the present investigation except that they did not report the presence of 20:3.[5,11,14] Pohl *et al.* reported[8] the fatty acid compositions of four Phaeophyta species but they did not find any 16:3, 16:4, 20:2, 20:3, or C_{22} polyolefinic acids. Cheucas

TABLE 4. FATTY ACID COMPOSITION OF

	% by weight										
	14:0	14:1	16:0	16:1 ω7+9	16:1 ω13t	16:2	16:3	16:4 ω3	18:0	18:1 ω9*	18:2 ω6
Laminaria saccharina											
MGDG	3·6	0·1	9·8	1·1	—	0·1	0·6	1·5	0·3	8·0	4·2
DGDG	2·4	0·2	14·7	3·8	—	0·1	0·7	0·3	2·4	10·3	1·6
Polar	7·5	0·2	23·0	3·3	2·0	0·1	tr.	tr.	0·9	13·8	7·4
Fucus spiralis											
MGDG	2·9	0·5	6·7	2·0	—	0·3	0·5	1·1	1·7	6·1	3·7
DGDG	4·5	0·6	9·3	1·8	—	0·3	1·2	0·4	0·9	10·0	3·9
Polar	11·9	0·4	21·7	0·6	1·2	0·3	0·8	tr.	0·9	14·6	6·2
Fucus serratus											
MGDG	2·5	0·2	6·3	0·6	—	0·2	0·6	4·8	1·0	5·9	3·9
DGDG	8·2	tr.	11·9	1·6	—	0·3	1·1	1·3	0·8	9·4	8·3
Polar	8·7	tr.	21·8	0·8	1·8	tr.	0·3	tr.	0·8	14·9	6·0
Ascophyllum nodosum											
MGDG	4·0	0·2	7·1	1·4	—	0·2	0·3	0·5	1·1	11·4	6·4
DGDG	6·3	0·1	9·4	1·8	—	0·2	0·6	0·1	1·0	17·1	5·4
Polar	14·1	tr.	21·4	1·1	2·1	0·2	0·5	tr.	0·4	17·7	6·5

tr.—trace.
* Other isomers present.

OF TOTAL LIPIDS OF PHAEOPHYTA

% by weight														
18:2 ω6	18:3 ω6	18:3 ω3	18:4 ω3	20:0 20:1	20:2 ω6	20:3 $\Delta^{5,11,14}$	20:3 ω6	20:4 ω6	20:4 ω3	20:5 ω3	22:0 22:1	22:4 ω6	22:5 ω3	22:6 ω3	24:0 24:1
5·4	1·2	10·1	26·0	0·1	0·2	—	0·4	6·7	0·7	24 2	0 4	0·1	0·6	tr.	0 1
6·8	0 4	8·9	8·9	0·3	0·3	—	0·4	9·1	0·4	19·3	0·3	tr.	0·2	tr.	tr.
4 9	0·6	9·0	15 8	1·1	0 1	—	0·1	9·5	0·5	18·3	0·3	tr.	0·5	tr.	0·2
11·9	1·2	7·4	12·0	0·2	0·2	—	0·6	12·4	0·6	10·4	0·1	tr.	tr.	tr.	tr.
14·6	1·1	9·5	7·7	2·4	0·3	0·1	0·3	12·0	0 4	4·8	0·1	tr.	0·2	tr.	tr.
6·3	1·7	10 2	16·4	0 2	0·1	tr.	0·4	19·1	0·5	18·6	0 1	tr.	0·2	tr.	tr.
7·8	1·6	11 2	14·5	0·5	0·1	—	0·9	14·5	0 7	14·2	0·1	0 2	0 8	0·3	0·2
6·9	1 0	7·3	14·2	1 1	0·1	—	0·6	8·1	0·8	22 8	0·1	0 1	0·2	0·6	0·1
13 7	0·6	6·9	6 3	0·7	0·1	—	0·7	8·5	0 5	9 8	tr.	tr.	tr.	tr.	0·1
3·9	0·6	9·9	20·3	0·1	0·2	—	0·2	9·2	0·7	28·4	0·1	tr.	0·2	tr.	0·2
2·8	0 5	6·7	19·3	0 4	0·1	—	0·4	12·6	1 1	24·8	0 1	tr.	tr.	tr.	0·1
4·2	0 9	10 6	27·9	0·7	tr.	—	0·4	11·9	0 4	18 4	tr.	tr.	tr.	tr.	tr.
7·3	0 7	7·3	6 8	1·2	0·4	0·4	0·8	14 2	0·5	7·1	0·6	0·3	0 8	tr.	0·3
7 4	0·4	8·8	11 4	0·3	0·6	0·3	0 1	13·1	0·3	12 3	0·8	0·1	0·6	0·3	0 2
8·1	0·7	5 0	2·2	0·5	0·8	0 5	0·8	13 0	0·2	6·9	0·6	tr.	0·1	tr.	0 2
9·1	0·5	7·8	7 8	0 9	0·7	0·4	0·8	13·3	0 5	15·7	0·5	tr.	1·9	tr.	0·1
8·0	0·3	10·2	11·0	0·4	0·5	0·2	0·4	17·0	0 4	19·5	0·8	tr.	1·0	tr.	0·8
9·6	0·6	6·1	4 3	0·9	0·1	0·1	1·1	12·4	0 5	5·8	0 2	0·1	0·4	tr.	0·2
9·1	0·4	10·8	9·7	0·3	0·4	0·1	0·9	13·1	0·4	11·0	0·8	0·1	0·2	tr.	0·1
7·9	0·3	4·0	4·3	0 5	2·5	3·0	2·8	9·6	0·3	5·2	0 7	0·4	1·2	0·3	0·3
7·7	0·2	5·1	4·4	0·2	2 0	4·2	0·3	13·2	0·8	8 8	0·8	0·2	0·6	0·1	0·2
10·4	1·3	6·0	3·5	0·4	1·3	0·8	1 9	16 5	0·1	6·2	0·4	0·2	0·8	tr.	0·2
10·1	1·1	3·2	1·3	0·4	0·6	0·3	2·0	13·6	0·1	5·2	0·5	0·3	1·0	0·2	0·4
10·5	0 8	3·2	1·1	0·3	0·7	0·2	1·8	13·6	0·4	7 4	0·5	0·2	0·8	0·1	0·2
6·1	0·6	9·9	12 6	0 3	0·2	—	0·5	22·8	1·1	9·0	0·1	tr.	tr.	tr.	0·1

and Riley[9] did not report 18:3, 18:4, or C_{16} and C_{22} polyolefinic acids in six Phaeophyta species and found 20:2 in only one of these. They did not find any 20:5ω3 in *F. vesiculosus* and *F. serratus* and only small amounts of this acid in the other four species.

The fatty acid compositions of different lipid classes of four Phaeophyta species are

DIFFERENT LIPID CLASSES OF PHAEOPHYTA

% by weight												
18:3 ω6	18:3 ω3	18:4 ω3	20:0 20:1	20:2 ω6	20:3 $\Delta^{5,11,14}$	20:3 ω6	20:4 ω6	20:4 ω3	20:5 ω3	22:0 22:1	Total ω3	Total ω6
0·9	4·9	44·7	0·5	tr.	—	0·1	1·2	0·1	18·0	0·3	69·2	7·1
0·2	16·5	18·6	0·3	tr.	—	tr.	4·5	0·1	22·6	0·6	58·1	7·1
0·2	12·0	2·1	0·6	0·1	—	0·5	13·7	0·2	11·7	0·7	26·0	22·0
0·6	11·7	31·2	0·1	0·1	tr.	0·2	7·2	0·3	22·7	0·4	67·0	12·6
0·4	10·5	22·2	0·4	0·1	tr.	0·2	6·7	0·1	25·1	1·2	58·7	12·8
0·3	14·4	0·8	0·3	0·5	tr.	0·6	17·4	0·2	5·3	1·6	20·7	26·1
0·5	15·6	24·9	0·5	0·1	0·5	0·5	8·6	0·5	21·5	0·8	67·3	14·4
0·4	10·9	10·9	tr.	0·5	tr.	0·9	10·6	0·5	16·2	1·7	44·4	22·1
0·2	12·4	1·7	0·5	0·1	0·1	0·6	20·8	0·3	6·9	1·7	21·3	28·7
0·5	11·1	22·0	tr.	1·2	2·6	0·2	6·5	0·9	21·2	1·2	55·7	15·3
0·3	12·1	13·8	0·3	0·4	0·5	0·6	5·2	1·0	22·5	1·3	49·5	12·7
0·2	5·6	0·6	0·3	3·1	tr.	3·5	17·4	0·1	4·4	1·2	10·7	31·4

TABLE 5. FATTY ACID COMPOSITION OF THE TOTAL LIPIDS OF CHLOROPHYTA

	% by weight							
	30 *Enteromorpha intestinalis*		31 *E. compressa*	32 *Ulva lactuca*		33 *Cladophora rupestris*		34 *C. albida*
Acid	Range†	Mean	Jul. 68	Oct. 68–Feb. 69		Range‡	Mean	Apr. 70
12:0	0·1–0·2	0·1	0·1	tr.	0·2	0·1–0·2	0·1	0 1
14:0	0·6–1·5	0·8	1·0	0·6	0·4	3·7–6·2	4·9	6·4
14:1	tr.–0·2	tr.	tr.	tr.	0·1	0·1–0·3	0·2	0·3
15:0	0·1–0 6	0 3	0·7	0·2	0·1	0·1–0·3	0·2	0·3
16:0	7·3–19·0	12·5	26·6	21·4	17·9	15·0–19·0	16·3	18·2
16:1ω7+9	0·8–2·4	1·6	1·7	3·1	0·4	10·5–13·3	11·9	15·2
16:1ω13t	0·7–1·3	1·0	0·6	3·5	1·7	1·9–3·0	2·2	1·1
16:2ω6	0·5–1·1	0·7	1·1	1·4	0 2	0 4–1·1	0·7	0·2
16:2ω4	0·1–0·2	0·1	0·2	0·1	0·1	2·0–3·0	2·5	0·8
16:3ω6	0·1–0·4	0·1	0·1	0·2	0·1	0·7–1·8	1·4	0·2
16:3ω4	0·1–0·4	0·1	0 5	0·2	0·1	0·4–0·8	0·6	0·2
16:3ω3	0·6–5·3	2·7	2·4	1·8	1·1	0·1–0·3	0·1	0 1
16:4ω3	10·0–23·2	15·5	7·2	13·9	17·2	11·8–17·4	15·3	6·9
16:4ω1	0·1–0·3	0·2	0·2	0·3	0·6	0·3–1·3	0·7	0·3
18:0	0·2–2·4	0·7	0·4	0·3	0·1	0·1–0·6	0·3	1·2
18:1ω9*	4·8–12·5	9·4	14·6	10·7	9·3	8·7–10·5	9·4	9·1
18:2ω6	3·8–8·5	5·6	11·7	5·6	1·6	13·1–18·1	15·1	3·1
18:3ω6	0·2–1·0	0·6	1·0	1·3	0·4	0·2–0·5	0·4	0·6
18:3ω3	14·1–25·2	20·8	14·2	16·2	16·7	1·1–3·2	2·3	14·0
18:4ω3	10·3–24·8	16·9	6·4	11·4	24·2	0·9–4·8	2·8	4·0
20:0 / 20:1	0·2–1·0	0·5	0·5	0·2	0·1	0·2–0·5	0·3	0·5
20:2ω6	0·1–0·5	0·2	0·2	0·1	0·2	0·2–0·4	0·3	0·1
20:3ω6	0·2–1·0	0·4	1·0	0·4	0·2	0·1–0·4	0·2	0·2
20:4ω6	0·4–2·1	1·4	2·0	2·1	0·5	2·1–2·9	2·5	1·8
20:4ω3	0·4–2·5	1·0	0·8	0·9	0·7	0·4–0·7	0·5	0·2
20:5ω3	1·1–4·8	2·3	2·0	1·3	2·1	4·0–8·0	6·3	12·0
22:0 / 22:1	0·4–1·5	0·7	0·7	0·3	0·6	0·1–0·3	0·2	0·3
22:4ω6	0·4–1·5	0·8	0·5	tr.	0·5	tr.–0·2	0·1	0·2
22:5ω3	1·1–4·2	2·6	1·0	1·6	2·2	0·8–1·8	1·3	1·9
22:6ω3	tr.–0·3	tr.	0·1	0·4	0·4	0·2–1·2	0·7	0·3
24:0 / 24:1	tr.–0·4	0·2	0·6	0·5	0·2	0·1–0·4	0·2	0·2

tr.—trace.
* Other isomers present.
† 10 samples taken between June 1967 and June 1970.
‡ 7 samples taken between July 1968 and March 1971.

given in Table 4. The highest concentrations of 16:4ω3, 18:4ω3 and 20:5ω3 are in the galactosyl diglycerides with 16:4ω3 and 18:4ω3 concentrated in the monogalactosyl diglycerides. The highest concentration of 20:4ω6 is in the polar lipids.

Chlorophyta

The fatty acid compositions, of five Chlorophyta species are shown in Table 5. The distribution of fatty acids is similar for the two Enteromorpha and the Ulva species. The major constituent acids are 16:0, 16:4ω3, 18:1, 18:2ω6, 18:3ω3 and 18:4ω3. The C_{20} acids are present in smaller amounts than in the Rhodophyta and the Phaeophyta. The *Clado-*

phora species are characterized in having high proportions of 16:1. *Cladophora rupestris* has much smaller proportions of 18:3ω3 and 18:4ω3 than the other Chlorophyta species studied but has similar amounts of 16:4ω3.

Our results for *E. compressa* are similar to those reported by Klenk *et al.*[7] These workers did not find 16:4ω3 in *Codium fragile* and Pohl *et al.*[8] found this acid in only two of five Chlorophyta species studied. Ackman *et al.*[1] found high amounts of 16:4ω3 in the lipids of the phytoplankton *Dunaliella tertiolecta* but Cheucas and Riley[2] did not detect this acid in *D. tertiolecta* and *D. primolecta* but did find significant amounts of the isomer, 16:4ω1.

The fatty acid compositions of different lipid classes of three Chlorophyta species are given in Table 6. In the three species 16:4ω3 is concentrated in the monogalactosyl diglycerides and in the two species with high proportions of 16:3ω3, this acid is concentrated in the digalactosyl diglycerides. In the two species with high proportions of 18:4ω3 and 18:3ω3, the former acid is concentrated in the monogalactosyl diglycerides and the latter in the digalactosyl diglycerides. In all three species 20:5ω3 is found in the three lipid classes with slightly higher proportions in the polar lipids. *Cladophora rupestris* differs from any of the marine algae studied in having high proportions of 18:2ω6 in the galactosyl diglycerides, this acid is usually concentrated in the polar lipids.

DISCUSSION

Our analyses show that the fatty acid compositions of marine algae are very complicated. There is a greater range of fatty acids present than in higher plants. Olefinic acids of the C_{14}, C_{16}, C_{18}, C_{20} and C_{22} series amount to over 70% of the total acids in most of the species studied; polyolefinic acids with up to five double bonds predominate. The saturated acids present are principally palmitic and myristic acids with smaller amounts of stearic acid and minor amounts of 12:0, 20:0, 22:0 and 24:0. The principal monoenoic acids are

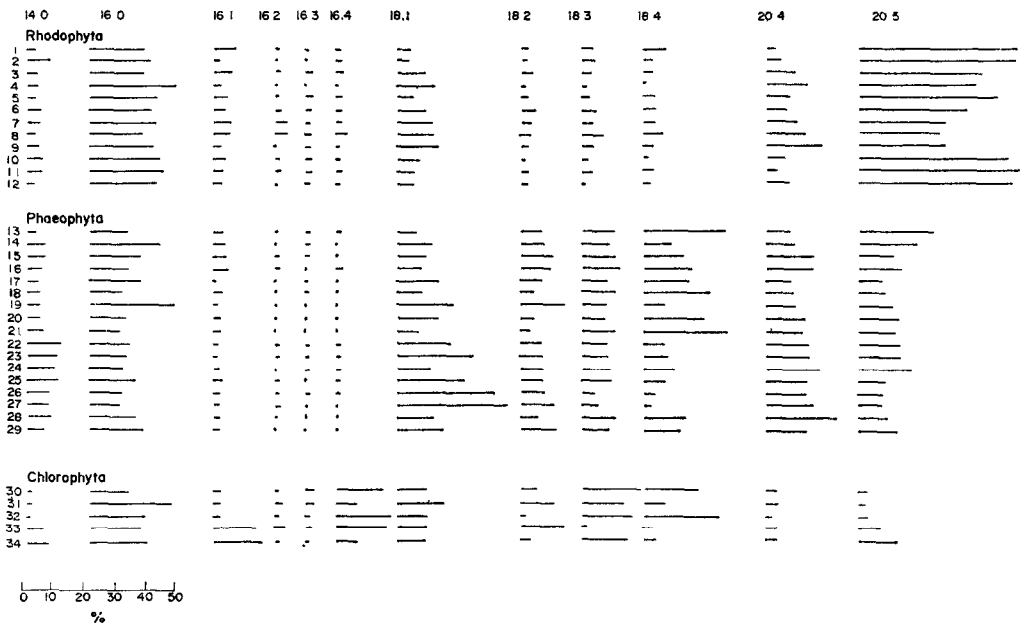

FIG. 1.

TABLE 6. FATTY ACID COMPOSITION OF

	% by weight											
	14:0	14:1	16:0	16:1 ω7+9	16:1 ω13t	16:2 ω6+4	16:3 ω6+4	16:3 ω3	16:4 ω3+1	18:0	18:1 ω9*	18:2 ω6
Enteromorpha intestinalis												
MGDG	0·3	0·1	3·0	0·6	—	0·5	0·4	3·1	30·7	0·2	2·5	2·4
DGDG	0·6	0·2	10·5	0·4	—	2·3	0·2	19·4	7·4	0·2	4·7	6·1
Polar	1·0	0·1	26·4	0·6	3·9	0·2	tr.	0·7	0·6	0·4	16·2	3·3
Ulva lactuca												
MGDG	0·5	tr.	1·9	0·6	—	0·1	0·1	0·6	43·5	tr.	2·3	0·7
DGDG	0·3	tr.	22·4	1·1	—	0·5	0·4	5·8	5·6	0·1	4·6	3·4
Polar	0·8	0·2	26·6	0·6	4·5	0·4	tr.	0·2	0·9	0·7	12·8	2·0
Cladophora rupestris												
MGDG	0·8	tr.	3·8	10·8	—	5·7	2·6	0·4	42·2	tr.	1·0	21·8
DGDG	3·2	tr.	24·9	10·3	—	3·5	1·8	0·4	15·3	0·1	4·7	22·2
Polar	7·8	tr.	25·5	11·0	3·7	1·3	1·3	0·5	0·8	0·3	12·1	8·5

tr.—trace.
* Other isomers present

16:1 and 18:1 and these are mixtures of isomers, mainly ω7 and ω9. The presence of the *trans* acid, 16:1ω13t, was demonstrated in every species studied and this acid has now been found in the lipids of green plants of widely different types. The major polyolefinic acids are usually of high unsaturation and in many of the Rhodophyta species, 20:5ω3 is present in amounts greater than 40%. High proportions of 16:4ω3 were found in the Chlorophyta species and, apart from algae, this acid has only been found in significant amounts in fish lipids. The variations in fatty acid distribution among Rhodophyta, Phaeophyta and Chlorophyta are shown in Fig. 1 and these variations may have taxonomic usefulness although more species would have to be examined and more data acquired on the seasonal variations of the fatty acid distributions.

It has been shown that, in the leaves of higher plants, there is a characteristic distribution of fatty acids in the galactosyl diglycerides, the main lipids of photosynthetic tissues:

(i) a variety of angiosperm species have both 16:3ω3 and 18:3ω3 in their leaf lipids and the sum of these ω3 acids amounts to 95 and 85% in the mono and digalactosyl diglycerides respectively. Also the lower molecular weight ω3 acid, viz. 16:3ω3, is concentrated in the monogalactosyl diglycerides and the highest concentration of 18:3ω3 is in the digalactosyl diglycerides;

(ii) Boraginaceae and Caryophyllaceae leaf lipids are unusual as they contain γ-linolenic and octadecatetra-6,9,12,15-enoic acids in addition to the usual acids found in angiosperm leaf lipids. The monogalactosyl diglycerides of *Myosotis scorpioides* (Boraginaceae) and *Stellaria media* (Caryophyllaceae) contain 86 and 91% respectively of $C_{18}\omega3$ acids and the digalactosyl diglycerides 56 and 86%. In these two species it is found that the ω3 acid with the higher unsaturation, viz 18:4ω3, is concentrated in the monogalactosyl diglycerides and the highest concentration of 18:3ω3 is in the digalactosyl diglycerides.

In the present investigation of the lipids of marine algae it is found that the monogalactosyl diglycerides are the most unsaturated and the polar lipids the least unsaturated (Table 7). The monogalactosyl diglycerides contain the highest proportions of ω3 acids and

DIFFERENT LIPID CLASSES OF CHLOROPHYTA

% by weight												
18:3 ω6	18:3	18:4	20:0	20:2	20:3	20:4	20:4	20:5	22:0	22:5	Total ω3	Total ω6
tr.	22·6	29·5	tr.	0·3	0·3	1·0	0·5	2·0	tr.	tr.	88·4	4·9
0·1	35·8	7·5	0·1	0·1	0·3	1·1	1·0	2·0	tr.	tr.	73·1	10·2
1·3	21·3	10·1	0·2	0·7	1·2	1·8	0·8	2·7	0·6	4·8	41·0	8·5
0·1	5·8	42·0	tr.	0·1	0·2	0·2	0·4	0·9	tr.	tr.	93·2	1·5
0·2	41·9	10·2	tr.	0·3	0·4	0·9	0·7	1·2	tr.	tr.	65·4	6·1
0·7	10·2	19·3	0·2	0·2	0·4	0·9	0·7	3·7	0·9	3·2	38·2	4·6
0·2	2·4	3·0	tr.	tr.	tr.	1·1	0·3	3·4	tr.	0·5	52·4	31·2
0·1	2·8	3·4	tr.	0·1	0·1	1·2	0·8	4·2	tr.	0·8	27·7	29·0
0·3	2·8	3·9	0·4	0·4	0·3	3·2	1·1	7·7	0·2	7·7	22·3	14·5

the polar lipids the highest proportions of ω6 acids and 16:1ω13t is only found in the polar lipids.

In those species which have high proportions of C_{16} and C_{18}ω3 acids, the acids with the highest unsaturation, *viz.* 16:4ω3 and 18:4ω3, are concentrated in the monogalactosyl diglycerides, and the less unsaturated acids, viz. 16:3ω3 and 18:3ω3 are found in highest concentrations in the digalactosyl diglycerides. In the Rhodophyta species which have

TABLE 7. DEGREE OF UNSATURATION OF THE FATTY ACIDS OF DIFFERENT LIPID CLASSES

	Average double bonds per mole fatty acid		
	MGDG	DGDG	Polar
Rhodophyta			
Corallina officinalis	3·8	3·0	2·6
Ceramium rubrum	3·0	2·2	1·9
Chondrus crispus	3·0	2·2	2·1
Phaeophyta			
Laminaria saccharina	3·1	2·7	1·8
Fucus spiralis	3·2	2·9	1·7
F. serratus	3·3	2·6	1·8
Ascophyllum nodosum	2·9	2·6	1·5
Chlorophyta			
Enteromorpha intestinalis	3·5	2·7	1·8
Ulva lactuca	3·7	2·4	2·1
Cladophora rupestris	2·9	1·9	1·6
mean:	3·2	2·5	1·9
Conifers[6]	2·8	2·5	1·7
Pteridophyta[11]	2·7	2·2	1·7
Angiosperms			
containing 16:3ω3[5]	2·9	2·7	1·9
containing 18:4ω3[3]	3·1	2·7	1·7

[11] G. R. JAMIESON, Ph.D. Thesis, Univ. of London (1970).

relatively small proportions of C_{16} and $C_{18}\omega3$ acids, $20:5\omega3$ is found in the highest concentrations in the monogalactosyl diglycerides but the other lipid classes also contain high proportions of this acid. In the Phaeophyta species, $20:5\omega3$ is found in the highest concentrations in both the mono- and digalactosyl diglycerides. In the Chlorophyta species which have high proportions of C_{16} and $C_{18}\omega3$ acids, both $20:5\omega3$ and $22:5\omega3$ are concentrated in the polar lipids.

EXPERIMENTAL

Samples of marine algae were collected from the shores of the Firth of Clyde at Seamill, Ayrshire. The algae were identified using a standard text[12] and verified by an algologist and botanist of the Biology Department.

Lipids were extracted and separated into classes by methods described previously.[3,11] GLC analyses 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]

[12] L. NEWTON, *A Handbook of British Seaweeds*, British Museum, Natural History (1931).
[13] G. R. JAMIESON, in *Topics in Lipid Chemistry* (edited by F. D. GUNSTONE), Vol. 1, Logos Press, London (1970).

Key Word Index—Rhodophyta; Chlorophyta; Phaeophyta; chemotaxonomy; fatty acids; galactosyl diglycerides.