

PHYCOCHEMICAL STUDIES ON FATTY ACID COMPOSITION IN *CAULERPA* (BRYOPSIDOPHYCEAE)

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Abstract

Four green seaweeds, *Caulerpa faridii* Nizamuddin, *C. racemosa* (Forsskal) J. Agardh, *C. scalpelliformis* (R. Brown) C. Agardh and *C. taxifolia* (Vahl) C. Agardh, collected from Buleji near Karachi were investigated phytochemically by gas chromatography – mass spectrometry. Saturated fatty acids were more (81.3 – 93.0%) than unsaturated ones with palmitic acid as the major component (76.8 – 87.9%). Oleic was the most commonly occurring unsaturated acid (2.5 – 4.5%) with diethenoids found in small quantity (1.8 – 3.7%). *C. taxifolia* differed in its fatty acid composition with other species.

Introduction

Lipids in algae have great significance because of their participation in biological membranes, their metabolic behaviour is largely determined by the structure of the component fatty acids. Much work has been done on fatty acids of micro-algae (Wood, 1974) with little information on the fatty acid composition of seaweeds (Qasim, 1986; Shameel, 1989). The present report describes the fatty acid composition of 4 species of *Caulerpa* collected from the coast of Karachi, Pakistan.

Materials and Methods

1. *Algal material and extraction.* Four different species of *Caulerpa* Lamouroux were collected partly from mid-littoral to upper sub-littoral rocks and pools at the rocky ledge and partly from sandy bay of Buleji, near Karachi during November 1988 and February 1989. They were thoroughly cleaned to remove sand particles and animal castings, dried in shade and passed through a mill. Dried seaweed, 1 kg, was extracted 3 times by percolation at room temperature with CHCl_3 : hexane (1:1) for 20 days and the extract evaporated under vacuum to obtain 50 g thick greenish residue.

2. *Saponification.* Ethanol and water (1:1) with 10% KOH was added to the residue and reaction mixture saponified by refluxing at 100°C for 8h. The mixture was concentrated under reduced pressure adding H_2O and Et_2O 3 times. The aqueous alkaline fraction was acidified with 6N HCl (pH 5-6) and then fractioned several times with Et_2O . The total Et_2O fraction was dried over anhydrous Na_2SO_4 , and on evaporation of Et_2O a residue (3-4g) was obtained.

3. *Esterification and GC – Mass spectrometry.* The fatty acid part weighing about 0.5 mg was dissolved in MeOH adding 0.5ml of diazomethane. The reaction mixture was kept overnight at (28°C) and evaporated under reduced pressure. The aliquotas were directly injected into GC – MS. Spectrometry of the methylated fraction of seaweeds was performed on GC – Hewlet Packard with a 11/73 DEC computer and a 1.2mx4mm packed glass column of Gas Chrom. Q (100-120 mesh, OV 101 1%). The column temperature was programmed between 70°C-250°C with a rate of increase of 8°C per min. The carrier gas (helium) flow rate was 32ml/min.

Results and Discussion

The individual fatty acids isolated and identified from *Caulerpa faridii* Nizamuddin, *C. racemosa* (Forsskal) J. Agardh, *C. scalpelliformis* (R. Brown) C. Agardh and *C. taxifolia* (Vahl) C. Agardh are presented in Table I. Saturated fatty acids were in much greater quantity (81.8-93.0%) than unsaturated fatty acids. Palmitic acid was the major component (76.8-87.9%) in all the 4 species of *Caulerpa*. It is the largest component in other green seaweeds as well (Usmanghani *et al.*, 1985; Qasim, 1986; Shameel, 1989). The identified saturated acids ranged from C12:0 to C18:0, with C17:0 missing. Green algae generally lack fatty acids with more than 18 carbon atoms (Wood, 1974). Unlike higher plants, the saturated acids of *Caulerpa* are low in molecular weight (M^{*}).

Among unsaturated fatty acids the monoethenoid acids were greater in quantity (4.5-16.2%) than the diethenoids (1.8-3.7%). Although unsaturated acids were present in small amount (6.8-18.0%), oleic acid was found in large quantity (2.5-4.5%) in *C. faridii*, *C. racemosa* and *C. scalpelliformis*, while decylacrylic acid was maximum (4.6%) in *C. taxifolia*. This may probably be due to differences in their habitat ecology since the former three species are found as epilithon on rocks, while *C. taxifolia* occurs in pools, sandy and muddy flats and also in sheltered and polluted areas and hence exhibits habitat variation (Nizamuddin, 1964; Shameel, 1978). Oleic acid has also been reported to occur in large proportion among ethenoids in other epilithic green seaweeds (Qasim, 1986; Shameel, 1989). The monoethenoids ranged from C11:1 to C20:1, with C14:1 and C15:1 missing. Among diethenoids linoleic acid was common in all the investigated species, while eicosadienoic acid was only found in *C. taxifolia*. Moreover, C18 is the only type of fatty acid, which occurred in the saturated, monoethenoid and diethenoid categories.

C. racemosa showed slightly more saturated fatty acids (93.0%) and less ethenoic acids (6.85%) than other species (81.7-84.4 and 15.5-18.0% respectively), and it lacks myristic acid. This may be due to its succulent and radial assimilator and very broad stolon (Nizamuddin, 1964). Generally *C. faridii*, *C. racemosa* and *C. scalpelliformis* exhibited a similar fatty acid composition, but *C. taxifolia* differed from other species practically in all the three categories of fatty acid composition (Table I). Lauric acid was to-

Table 1. Relative percentages of fatty acids in *Caulerpa* species.

Fatty acid	Systematic Name (Common Name)	Mol. Form. (M ⁿ)	<i>C. faridii</i>	<i>C. racemosa</i>	<i>C. scalpelliformis</i>	<i>C. taxifolia</i>
	A. Saturated fatty acids:		81.87	93.06	84.09	84.43
C12:0	Dodecanoic acid (Lauric acid)	C ₁₂ H ₂₄ O ₂ (200)	2.68	1.03	2.39	—
C13:0	Tridecanoic acid (Tridecylic acid)	C ₁₃ H ₂₆ O ₂ (214)	—	1.37	—	1.43
C14:0	Tetradecanoic acid (Myristic acid)	C ₁₄ H ₂₈ O ₂ (228)	0.25	—	0.47	0.61
C15:0	Pentadecanoic acid (Pentadecylic acid)	C ₁₅ H ₃₀ O ₂ (242)	—	0.83	—	0.72
C16:0	Hexadecanoic acid (Palmitic acid)	C ₁₆ H ₃₂ O ₂ (256)	76.83	87.98	78.82	80.78
C18:0	Octadecanoic acid (Stearic acid)	C ₁₈ H ₃₆ O ₂ (284)	2.11	1.85	2.41	0.89
	B. Monoethenoid fatty acids:		16.24	4.47	13.87	11.77
C11:1	Undecenoic acid (Undecylenic acid)	C ₁₁ H ₂₀ O ₂ (184)	2.29	—	1.57	—
C12:1	Dodecenoic acid (Lauroleic acid)	C ₁₂ H ₂₂ O ₂ (198)	1.40	0.92	1.23	1.45
C13:1	Tridecenoic acid (Decylacrylic acid)	C ₁₃ H ₂₄ O ₂ (212)	—	—	—	4.63
C16:1	Hexadecenoic acid (Palmitoleic acid)	C ₁₆ H ₃₀ O ₂ (254)	3.76	—	3.52	1.52
C18:1	Octadecenoic acid (Oleic acid)	C ₁₈ H ₃₄ O ₂ (282)	4.57	2.51	4.21	2.28
C20:1	Eicosenoic acid (Gadoleic acid)	C ₂₀ H ₃₈ O ₂ (310)	4.22	1.04	3.34	1.89
	C. Diethenoid fatty acids:		1.83	2.38	1.96	3.75
C18:2	Octadecadienoic acid (Linoleic acid)	H ₁₈ H ₃₂ O ₂ (280)	1.83	2.38	1.96	2.52
C20:2	Eicosadienoic acid	C ₂₀ H ₃₆ O ₂ (308)	—	—	—	1.23

tally absent in *C. taxifolia*, though it was present in other species (1.0-2.6%). Stearic acid, though found in small quantity (1.8-2.4%) in other species, was found only in traces (0.8%) in *C. taxifolia*. The range of occurrence of saturated fatty acids in *C. taxifolia* may be narrowed down between C13:0 and C16:0 (see above). Decylacrylic and eicosadienoic acids were completely absent in other species, but they were found 4.63 and 1.23% respectively in *C. taxifolia*. Unlike other species oleic acid is present in this seaweed in small proportion (only 2.2%). *C. taxifolia* also differs from *C. faridii* and *C. racemosa* in having comparatively larger amount of total lipids and glycerides and smaller amount of sterol (Qasim, 1986). These differences may be due to a different metabolic behaviour of this species, which might have been caused by its habitat variation.

Acknowledgements

We gratefully acknowledge the valuable help rendered by Dr. K. Usmanghani, Associate Professor, Department of Pharmacognosy and Dr. (Mrs.) Shaheen Bano, Research Associate, H.E.J. Research Institute of Chemistry, University of Karachi during the course of this study.

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(Received for publication 15 May 1989)