Chemical Profiling of Seaweeds from the Karachi Coast using GC - MS

Munawwer Rasheed[1], Afshan Yasmeen[2], Pirzada Jamal Ahmed Siddiqui[2], Amir Ahmed[3], Muhammad Nadir[4], and Aasma Hashmi[5]

[1]Centre of Excellence in Marine Biology (CEMB), and
Department of Chemistry, University of Karachi, Karachi, Pakistan
[2] Centre of Excellence in Marine Biology (CEMB), University of Karachi, and
National Institute Maritime Affairs, Bahria University, Karachi Campus, Karachi, Pakistan
[3]PRC, PCSIR, Karachi Laboratory Complex, Karachi, Pakistan
[4]Government Degree Boys college, Sector-5/L, New Karachi, Pakistan
[5]Department of Chemistry, University of Karachi, and
Jinnah University for Women, Karachi, Pakistan
E-mail: rasheed.munawwer@uok.edu.pk

ABSTRACT

Introduction: The ability of marine algae to produce bioactive compounds with immense properties has now been established and has recently been intensively exploited particularly for pharmaceutical applications. The diversity of these compounds produced by seaweeds is outstanding and has demonstrated a variety of biological activities Currently algae represent about 9% of biomedical compounds obtained from marine sources. Volatiles e.g., fragrance are released by the living being directly in surrounding environment. In current study, *Sargassumwightii* (sargassceae) harvested from the Karachi coast was subjected to antioxidant activity and GC-MS analyses for analyzing different constituents present in these botanicals. Only few studies have been reported in literature**.**

Objective: To identify the metabolites, present in the botanicals obtained from the *S.wightiiexploiting* GC-MS

Methodology: Fresh specimens, collected from the coastal area (Sandspit) of Karachi, were cleaned from epiphytes, rinsed with distilled water to remove any associated debrisand air-dried in shade.Seaweed fronds were ground into fine powder, percolated at room temperature in 70% MeOH thrice. All extracts were combined, filtered, and evaporated under vacuum resulting in crude methanol extract (CM001). Semi-solid residue of CM001was shaken with n-hexane and kept for soaking overnight thrice. Hexane soluble portions were filtered, dried, and evaporated to obtain hexane fraction (H001).

Gas chromatography with FID was performed on Shimadzu GC-9A. Gas chromatography - mass spectrometric (GC-MS) was performed using a Shimadzu QP2010 with quadrupole detector. HP-5® fused silica capillary column (30 m x 0.25 mm i.d. x 0.25 μmdf) with helium as carrier gas was used.

Conclusion/Results: GC-MS profileofall fractions (H001, D001, M001, S001, and methylated products of S001 (SE001 and SC001) revealed the presence of 102 constituents among these 81 were identified, including 33 natural constituents belonging to various classes of natural compounds and 48 bio accumulated compounds. Current study was designed for naturally volatile, non-polar to moderately polar constituents but has revealed the presence of these contaminants. Qualitatively, H001 was the most productive extract resulting in identification of 61 constituents. Quantitatively, these identifications were ~50% of composition. D001 with 32 identifications comprising 82% composition was the second most productive extract. Quantitatively, extract SC001 obtained from the reaction mixture after methylation of Soxhlet extract (S001) was the most productive 99.7% of constituents were identified by composition however, the numbers of

constituents were just 24. SE001 obtained separately from same methylation reaction mixture using petroleum ether also showed 24 constituents (98.6% by composition).

Comprehensive analyses showed presence of 23 fatty acids in all. These included Methyl laurate (**25**), methyl myristate (**33**) and myristic acid (**34**), methyl iso-pentadecanoate (**37**), methyl pentadecylate (**40**), isopropyl myristate (**41**), methyl palmitoleate (**46**) and palmitoleic acid (**49**), methyl palmitate (**47**) andpalmitic acid (**51**), methyl margarate (**52**), methyl linoleate (**54**), methyl oleate (**55**) and Oleic acid (**59**), methyl elaidate (**56**), methyl stearate (**58**), methyl 9Z,12E-Octadecadienoate (**60**), methyl arachidonate (**63**), gondoic acid (**64**), methyl arachidate (**65**), methyl erucate (**69**), methyl behenate (**70**), and methyl lignocerate (**75**). Of these, **37**, **40**, **41**, **56**, and **60** are identified for the first time from this species.Palmitic acid (**51**) is the most abundant saturated fatty acid in nature, with palm oil as its main source. 51 is also the most abundant fatty acid in this study. All other identified fatty acidshave been reported from various sources including seaweeds (Figure **1**).

Beside fatty acids, 10 other natural metabolites were also identified in current study. These included 2 fatty aldehydes; nonanal (**16**) and 2E-decenal (**20**); 2 fatty alcohols, lignocerol (**68**) and pentacosyl alcohol (**73**); four isoprenoids, phytane (**36**), iso-phytol (**42**), hexahydrofarnesyl acetone (**43**), and *E*-phytol (**57**), and 2 phytosterols, β-Sitosterol (**79**) and fucosterol (**81**).

The bioaccumulated compounds identified in the current study can be categorised in three distinct classes of pollutants i.e., petrochemicals, cyclosiloxanes,and plasticizers.

In current study, a series of well-known pollutants have been identified. Certain aliphatic hydrocarbons are reported as natural constituents and are well supported by biosynthetic routes. The current study has resulted in the identification of 28 petrochemicals, including 17 aliphatic hydocarbons, 6 aromatic hydrocarbons and 5 oxygenated hydrocarbons. Identified aliphatic hydocarbons (Figure-**2**) include 2,4-dimethyl-hexane (1), n-decane (**14**), n-undecane (**15**), n-dodecane (19), n-tetradecane (**22**), n-pentadecane (**24**), n-hexadecane (**27**), 7-methyl-hexadecane (**29**), 3-methyl-hexadecane (**30**), n-heptadecane (**31**), 2-methyl-heptadecane (iso-octadecane) (38), n-octadecane (39), n-nonadecane (**45**), 2-methyl-docosane (**62**), n-heptacosane (**74**), 2-methyl-octacosane (**77**), and n-dotriacontane (**80**). Of these **14, 15, 19, 22, 24, 27, 31, 39, 45**, and **74** are authenticated by the retention time also because these were the part of standard mixture injected and used in calculating KI.

Current study has also revealed 6 aromatics. These include; methyl-benzene (toluene) (**2**), phenyl-ethane (ethyl benzene) (**7**), either 1,3-dimethyl benzene (*m-xylene*) or 1,4-dimethyl benzene (*p-xylene*) (8), 1-ethyl-4-methyl-benzene (4-ethyl-toluene) (**11**), 1-ethyl-2-methyl-benzene (2-ethyl-toluene) (12), and 1,2,4-trimethyl-benzene (pseudo-cumene) (**13**).

REFERENCES

1. Ph.D. dissertation of Ms. Afshan Yasmeen, submitted to the HEC repository in 2017, entitled “Phytochemical studies on major drifted seaweed secies” supervised by Munawwer Rasheed and co-supervised by Pirzada Jamal Ahmed Siddiqui.
2. Yasmeen, M. Qasim, A. Ahmed, Nizam Uddin, Zeeshanahmed, M. Shaiq Ali, and M. Rasheed, GCMS and antioxidant Studies on Botanicals from Sargassumwightii: Natural Product Study Revealing Environmental Contaminants, Journal of the Chemical Society of Pakistan, 40 (1), 2018, 201-212.