Hydrocarbons of marine phytoplankton*

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Abstract

The hydrocarbon contents of 23 species of algae (22 marine planktonic), belonging to 9 algal classes, were analyzed. The highly unsaturated 3,6,9,12,15,18-heneicosahexaene predominates in the Bacillariophyceae, Dinophyceae, Cryptophyceae, Haptophyceae and Euglenophyceae. *Rhizosolenia setigera* contains n-heneicosane, presumably derived from the hexaolefin by hydrogenation. Two isomeric heptadecenes have been isolated: the double bond is located in 5-position in the blue-green alga *Synechococcus bacillaris* and in 7-position in 2 green algae. Our complete analyses are discussed in the context of earlier data; some generalizations appear no longer valid. Hydrocarbon analysis of marine algae should provide a tool for the investigation of the dynamics of the marine food chain. Knowledge now available provides the background needed for distinguishing between hydrocarbons of recent biogenic origin and hydrocarbon pollutants from fossil fuels.

Introduction

Ocean waters, marine organisms and sediments contain hydrocarbons which are derived from many sources. Biogenic hydrocarbons are essential components or adventitious byproducts of biochemical syntheses; they occur in all organisms. Fossil hydrocarbons, which were formed or altered by reactions in sediments, may reenter the ocean as submarine seepage or in the form of pollution. We have shown that hydrocarbons, even highly unsaturated ones, are remarkably stable in the marine food chain (BLUMER, 1967; BLUMER et al., 1970a, b). This stability, and the great variability of the hydrocarbon composition of different sources, suggests the possibility of using hydrocarbon analysis as a tool in the investigation of dynamic processes in the marine food chain.

Hydrocarbon analysis can also be a valuable tool in studies of the spread and eventual fate of marine pollutants. For tracing oil pollution it is not sufficient to analyze the total hydrocarbon content of marine specimens. A more extensive characterization and a separation of the complex hydrocarbon mixture into individual components is necessary for distinguishing

between hydrocarbons of recent biogenic origin and hydrocarbons from fossil fuels.

However, to realize the potential of these concepts, we need a more extensive characterization of the hydrocarbons in primary marine sources. Rather extensive data exist on the hydrocarbon composition of marine zooplankton (BLUMER et al., 1963, 1964, 1969, 1970a; BLUMER and THOMAS, 1965a, b); in contrast, data on the hydrocarbons in marine phytoplankton are scarce, and are limited either in the scope of chemical structures which were analyzed or in the coverage of algal classes (CLARK and BLUMER, 1967; GELPI et al., 1968, 1970; HAN et al., 1968; MAXWELL et al., 1968; STRANSKY et al., 1968; HAN and CALVIN, 1969; WINTERS et al., 1969).

We have now analyzed representatives of the principal classes of marine phytoplankton for their hydrocarbon content in the C_{12} to approximately C_{25} range. The structures of the predominant hydrocarbons have been determined by combining gas chromatography with mass spectrometry and with chemical techniques. This work was carried out in conjunction with a study of a C_{21} hexaolefin in the marine food chain (BLUMER et al., 1970a) and represents a survey that should be complemented by the analysis of additional species and by a study of the variability of the hydrocarbon composition of algae grown under different environmental or nutritional circumstances.

Material and methods

Specimens, culture conditions and experimental techniques are those described by BLUMER et al. (1970a). The identity of the straight chain alkanes was established from their gas chromatographic retention indices on Apiezon L and FFAP (Varian Aerograph) and, in some cases, by mass spectrometry. Abundant alkenes were trapped from the gas chromatographic effluent and analyzed by retention index before and after hydrogenation, by mass spectrometry and by ozonolysis followed by gas chromatography and mass spectrometry.

Results

On ozonolysis, the major olefin of *Synechococcus* produced n-pentanal and n-dodecanal as major fragments, while the predominant olefin of *Dunaliella*, *Derbesia* and clone GSB Sticho yielded principally n-heptanal and n-decanal. Minor alkenes were analyzed only by the measurement of the retention index before and after hydrogenation; in these cases no assignment of double bond positions is yet possible.

Our techniques detected hydrocarbons in the C_{14} to C_{25} range; occasionally, hydrocarbons boiling as low as dodecane were found by gas chromatography.

Table 1. *Hydrocarbons in planktonic algae*

Class and species[a]	Predominant hydrocarbons[b]	Trace hydrocarbons[c]
Bacillariophyceae		
Cyclotella nana (3H)	$n\text{-}C_{21}{:}6^d$	pristane, n-p (low)
Ditylum brightwellii (D. Bright.)	$n\text{-}C_{21}{:}6^d$	n-p, low
Lauderia borealis (Clone 14)	$n\text{-}C_{21}{:}6^d$	n-p
Rhizosolenia setigera (Rhizo)	$n\text{-}C_{21}$, $n\text{-}C_{17}$, $n\text{-}C_{21}{:}6^{d,\,e}$	pristane, n-p
Skeletonema costatum (Skel)	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Thalassiosira fluviatilis (Actin)	$n\text{-}C_{21}{:}6^d$	pristane, n-p, $n\text{-}C_{21}{:}4(?)$
Thalassiosira sp.	$n\text{-}C_{21}{:}6^d$	pristane, n-p, $n\text{-}C_{21}{:}4(?)$
Dinophyceae		
Gonyaulax polyedra (GP 60e)	$n\text{-}C_{21}{:}6^d$	n-p
Gymnodinium splendens (Gym. s.)	$n\text{-}C_{21}{:}6^d$	n-p, low
Peridinium trochoideum (Peri)	$n\text{-}C_{21}{:}6^d$	n-p
Peridinium trochoideum, old culture	$n\text{-}C_{21}{:}6^d$, $n\text{-}C_{17}$, $n\text{-}C_{15}{}^e$	n-p
Cryptophyceae		
Cryptomonas (Rhodomonas?) sp. (3C)[f]	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Cryptomonas (Rhodomonas?), old culture	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Haptophyceae		
Coccolithus huxleyi (BT-6)	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Isochrysis galbana (Iso)	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Pheaocystis poucheti (Pp)	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Pheaocystis poucheti (677-3)	$n\text{-}C_{21}{:}6^d$	pristane, n-p
Euglenophyceae		
Eutrepiella sp. (W.H. Eut.)	$n\text{-}C_{21}{:}6^d$, $n\text{-}C_{17}$, $n\text{-}C_{15}{}^e$	pristane, n-p
Cyanophyceae		
Oscillatoria woronichinii (Sm 24)	e	e
Synechococcus bacillaris (Syn.)	e	e
Rhodophyceae		
Porphyridium sp. (Porph)	e	e
Xanthophyceae		
Tribonema aequale (No. 50)[g]	e	e
Undetermined sp. (GSB Sticho)[h]	e	e
Chlorophyceae		
Dunaliella tertiolecta (Dun.)	e	e
Derbesia tenuissima (LB 1260)	e	e

[a] See BLUMER et al. (1970b) for source.

[b] $n\text{-}C_{21}{:}6$ is 3,6,9,12,15,18-heneicosahexaene (presumed all *cis*), $n\text{-}C_x$ is normal alkane of x carbon atoms.

[c] n-p designates normal alkane content, usually at low level from about C_{14} to C_{25} without marked predominance of individual alkanes.

[d] For concentration and predominance of $n\text{-}C_{21}{:}6$ see BLUMER et al. (1970a).

[e] Details in Fig. 1, this paper.

[f] Now believed to be a species of *Chroomonas*.

[g] A freshwater algae, studied because of its clear taxonomic position. No certain marine xanthophytes are available.

[h] Systematic position uncertain. May belong to the new class Eustigmatophyceae.
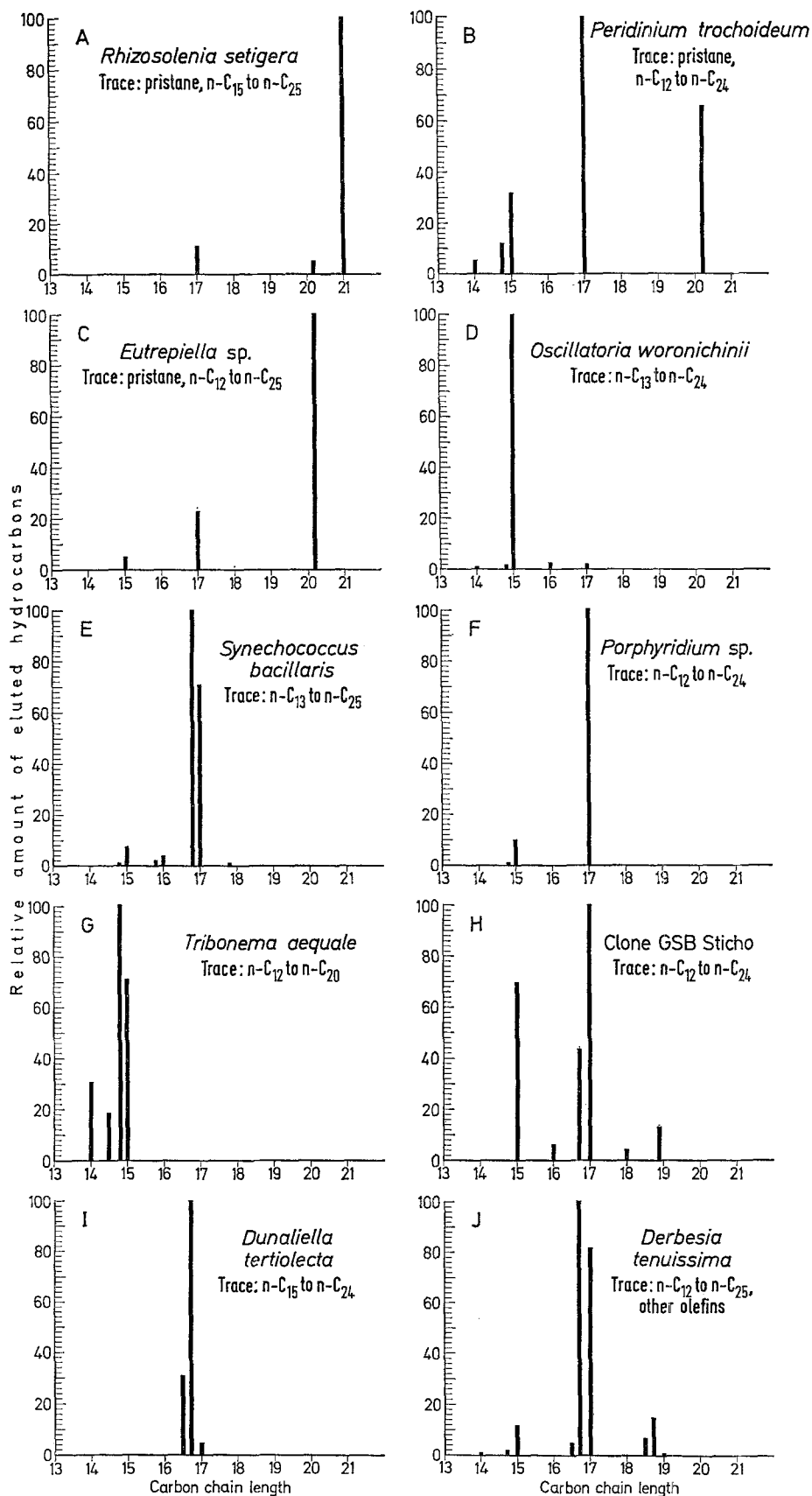
Fig. 1. Normalized gas chromatograms of algal hydrocarbons on Apiezon L. Chromatograms of algae whose sole major component is HEH (Table 1) are not reproduced. Represented is the elution sequence on an unpolar column. Peaks at whole numbers represent n-alkanes of corresponding carbon number. Peaks of intermediate position represent n-alkenes whose carbon number corresponds to the next higher whole number. Unsaturation increases with increasing distance from the next higher whole number. The assignments have been confirmed by gas chromatography on the polar substrate FFAP and, for major compounds, by mass spectrometry

We feel that findings of hydrocarbons below C_{14} are real, but no quantitative figures can be given because of the probable loss of these low boiling hydrocarbons during sample preparation. Only insignificant amounts of hydrocarbons were found above C_{21}; Fig. 1 is, therefore, limited to the C_{14} to C_{21} range. Results are set forth in Table 1 and Fig. 1.

Discussion

The hydrocarbons of planktonic algae are few, and of simple structure compared to those of ancient sediments and fossil fuels. Crude oil contains a wide range of isomeric structures covering many homologous series, it is rich in isoparaffins, cycloalkanes, and aromatics, but contains no olefins. Algae, on the other hand, contain normal paraffins, often with one or two compounds exceeding all others by orders of magnitude; they are rich also in olefins, but contain only few isoparaffins and few, if any, cycloparaffins and aromatics.

The olefins of phytoplankton and of zooplankton are markedly different. Copepods contain characteristic assemblages of C_{19} and C_{20} isoprenoids, both saturated and unsaturated; they are derived from the phytol which is present in their food. While the saturated C_{19} isoprenoid pristane is a common minor component of algae, we have been unable to detect the corresponding olefins.

There is a general uniformity of hydrocarbon composition within the major algal groups, our analyses (Table 1; Fig. 1) are, therefore, discussed in their taxonomic context.

Bacillariophycea

The outstanding characteristic of most centric diatoms is the predominance of a single olefinic hydrocarbon, all-*cis*-3,6,9,12,15,18-heneicosahexaene ($C_{21}H_{32}$, HEH). The isolation, identification and relative abundance of HEH in algae have been discussed by BLUMER et al. (1970a). The structural similarity of HEH and all-*cis*-docosahexaenoic acid and the simultaneous occurrence or absence of both in various species of algae suggest that one is biochemically derived from the other. In addition to HEH, the centric diatoms contain traces of paraffins in the C_{15} to C_{25} range, and pristane occurs at similarly low concentrations.

The only centric diatom with markedly different hydrocarbon composition was *Rhizosolenia setigera* (BLUMER et al., 1970a), in which n-heneicosane ($C_{21}H_{44}$) predominates over n-heptadecane and HEH; pristane and normal paraffins from C_{15} to C_{26} are minor components. Heneicosane in *R. setigera* might be a hydrogenation product of HEH, or a decarboxylation product of docosanic acid ($C_{21}H_{43}COOH$). We prefer the former explanation, since the possible precursor,

docosanic acid, is absent in centric diatoms (ACKMAN et al., 1968).

Gas chromatograms of sufficiently large hydrocarbon extracts from *Thalassiosira fluviatilis* reveal a minor peak at the retention indices 2064 (Apiezon L) and 2310 (FFAP). The difference between the retention indices on these non-polar and polar phases, ΔI, is $^2/_3$ that measured for HEH (ΔI 246 versus 368). This suggests the presence in *T. fluviatilis* of a C_{21} tetraolefin, which might be derived from HEH through partial hydrogenation by a process similar to that which produces the fully saturated heneicosane in *Rhizosolenia setigera*.

Dinophyceae, Cryptophyceae, Haptophyceae and Euglenophyceae

These algae have a hydrocarbon distribution pattern very similar to that of the centric diatoms. HEH is always predominant, and straight chain paraffins in the C_{15} to C_{25} range are present at low concentrations. Only in *Eutrepiella* were heptadecane and pentadecane found at appreciable concentrations.

The effect of the age of the cultures on HEH content has been studied for *Cryptomonas* (BLUMER et al., 1970a) and a similar observation has now been made for *Peridinium*. In a 12 day old culture (cell density 2×10^4/ml), HEH far exceeded the concentration of any other hydrocarbon. During extended growth for a total of 17 days (cell density 5×10^4/ml) the culture went into stationary phase; this resulted in predominance of heptadecane over HEH (Fig. 1) pentadecane and tetradecane were then present at appreciable concentration and a peak in the gas chromatogram at retention index 1475 (Apiezon L) was tentatively identified as a pentadecene. The observations on *Cryptomonas* and *Peridinium* suggest that effective synthesis or storage of HEH may not continue beyond the logarithmic growth phase.

Rhodophyceae, Xanthophyceae and Chlorophyceae

The hydrocarbon composition of these, and of the blue-green algae, is very different from that of the classes discussed above. Other olefins may take the place of HEH, which is completely absent; within the saturated hydrocarbon series, n-pentadecane or n-heptadecane predominate.

The red alga *Porphyridium* contains traces of straight chain alkanes from C_{12} to C_{24}; within this range, n-heptadecane predominates and n-pentadecane is quite abundant. A minor gas chromatographic peak (retention index 1475, Apiezon L) suggests the presence of a pentadecene. Additional red algae will have to be analyzed to decide whether the low abundance of olefins is characteristic of this class.

In the gas chromatogram of *Tribonema*, few hydrocarbons are evident outside the C_{12} to C_{15} range. The

major constituent is a pentadecene, followed by pentadecane, tetradecane and a presumed pentadecadiene.

The gas chromatogram of clone GSB Sticho is more complex. N-heptadecane and n-pentadecane predominate. The major olefinic hydrocarbon (retention indices 1668 and 1725 on Apiezon L and FFAP) has been identified by ozonolysis and GC-MS as 7-heptadecene. Another minor component (indices 1890 and 1954 on Apiezon L and FFAP) may be a nonadecene. Gas chromatography and mass spectrometry of the total hydrocarbons provides no evidence for minor di- and triolefins.

The major component of *Dunaliella* is 7-heptadecene. Retention indices (1650 and 1760 on Apiezon L and FFAP) and mass spectra characterize the second most abundant hydrocarbon as a heptadecadiene; double bond positions have not yet been established. Mass spectra of the ascending part of this peak, when eluted from Apiezon L, demonstrate the presence of small amounts of a C_{17} triene and of traces of a C_{17} tetraene. Another trace component (retention indices 1769 and 1817 on Apiezon L and FFAP) may be an octadecene. In *Dunaliella*, straight chain paraffins are minor components, among these n-heptadecane predominates and n-pentadecane just exceeds the general paraffin background.

Derbesia contains straight chain alkanes extending from C_{12} to C_{26}; heptadecane and pentadecane predominate within this group. The major hydrocarbon is again 7-heptadecene, accompanied by a smaller amount of a C_{17}-diene. Gas chromatography also suggests the presence of nonadecene, of nonadecadiene and of a small amount of pentadecene. Double bond positions have not been established.

Cyanophyceae

The hydrocarbon composition of the two blue-green algae we analyzed, somewhat resembles that of the 3 algal classes just discussed. However, there are some significant differences.

In *Oscillatoria*, n-pentadecane is present in high abundance, followed by the n-C_{16}, n-C_{17} and n-C_{14} alkanes which extend above a very low n-alkane background from C_{13} to C_{24}. The presence of a pentadecene is suggested from the gas chromatograms. Branched hydrocarbons or abundant high boiling alkanes are not indicated.

The principal hydrocarbon of *Synechococcus* is a heptadecene[1]; ozonolysis followed by gas chromatography and mass spectrometry proves that the double bond is in 5-position, in contrast to the 7-heptadecane in the green algae. The normal alkanes, with 15, 16 and 17 carbons, are abundant and C_{15} and C_{16} monoolefins occur at low concentrations. A minor peak at retention index 1775 (Apiezon L) may be of a complex nature,

the mass spectrum shows the presence of an octadecene (molecular ion: m/e 252); however, the corresponding peak in the Apiezon chromatogram does not completely disappear after hydrogenation. This suggests the possible presence of traces of a branched octadecane. The mass spectra measured in the ascending region of the heptadecene peak suggest the presence of traces of di-, tri- and tetraolefins (molecular ions: m/e at 236, 234 and 232).

Hydrocarbons in our cultures of *Oscillatoria* and *Synechococcus* differ from those in most of the other species of blue-green algae which have been studied (GELPI et al., 1968, 1970; HAN et al., 1968; WINTERS et al., 1969). The latter algae showed a general predominance of n-heptadecane, with n-pentadecane, n-hexadecane, or one of several isomeric methylheptadecanes next in abundance (except in *Anacystis montana*, referred to again later). Olefins were absent or made up less than 5% of the total hydrocarbons in this group. However, there was another group, consisting of 3 isolates of marine coccoid blue-green algae, in which nonadecene predominated, accompanied by small amounts of nonadecadiene. In this second group, n-heptadecane was not detected (WINTERS et al., 1969). It is noteworthy that one of the algae in the first group, *Anacystis montana*, is also a coccoid form, and it had a high content of mono-, di-, and triolefins in the C_{21}-C_{27} range. Our coccoid form (the *Synechococcus*) contains the olefin heptadecene in abundance and others in small amounts.

Conclusions

In their most recent paper, GELPI et al. (1970) warn against premature correlation of molecular complexity with evolutionary development, since phylogenetic comparisons appear to be justified only within a limited taxonomic grouping.

Our findings support this cautions statement. The hydrocarbons which at present seem to be most definitely located in distinct phylogenetic position are the heneicosahexaene and heneicosane found in the golden-brown group of algae, in the cryptomonads, and in the euglenids; the 5-heptadecene in *Syneccho-coccus*; the nonadecene found in certain coccoid blue-green algae, the branched methylalkanes occurring in most blue-green algae, and the 7-heptadecene found in green algae and the clone GSB Sticho, which is of uncertain systematic position.

Specifically, some earlier generalizations appear no longer valid. Thus, HAN and CALVIN's (1969) statement, that normal heptadecane is the dominant hydrocarbon of all photosynthetic microorganisms, is not confirmed. As we found earlier for benthic algae (CLARK and BLUMER, 1967) pentadecane may predominate over heptadecane; also, olefinic hydrocarbons may far overshadow the contribution of saturated compounds to the algal hydrocarbons.

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[1] Retention indices 1679 (Apiezon) and 1733 (FFAP).

Pristane and squalene, thought to be absent in algae (HAN and CALVIN, 1969), have been identified in benthic and planktonic algae (CLARK and BLUMER, 1967; GELPI et al., 1970; and the present paper).

The 6-, 7- and 8-methylbranched heptadecanes reported as major compounds of blue-green algae by HAN et al. (1968) and GELPI et al. (1970) were not encountered in our analyses, with the possible exception of a minor occurrence in *Synechococcus*.

The analytical finding of hydrocarbons below tetradecane and above tricosane, assumed to occur rarely in blue-green and green algae (HAN and CALVIN, 1969), and the discovery of a second hydrocarbon mode in the C_{25} to C_{33} range (GELPI et al., 1968, 1970) suggests that these hydrocarbons might have been overlooked in earlier analyses because of analytical limitations.

GELPI et al. (1968, 1970) distinguish 2 distinct groups of algae, one containing only lower boiling hydrocarbons, the other low and high boiling hydrocarbons. The species analyzed here appear to belong to the former group, unless some should contain hydrocarbons beyond C_{26}, our analytical limit.

Our limited experience with algae harvested at different growth stages *(Cryptomonas, Peridinium)* urges further caution in the interpretation of evolutionary trends in algal hydrocarbon content.

Many species or classes of algae have a sufficiently characteristic hydrocarbon composition to permit the chemical detection of their presence in mixed plankton samples; similar analyses of the lipids of zooplankton might reveal the specific sources of their lipids. The simple and characteristic hydrocarbon composition of algae can be recognized even in the presence of considerable contamination with hydrocarbons derived from fossil fuels.

Summary

1. The hydrocarbon content of 22 species of marine planktonic algae (and one fresh-water form) belonging to 9 algal classes was analyzed.

2. Ozonolysis, gas chromatography and mass spectrometry established the presence of 5-heptadecene in the blue-green alga *Synechococcus bacillaris*, of 7-heptadecene in the green algae *Dunaliella tertiolecta* and *Derbesia tenuissima* as well as in the clone GSB Sticho, which is of uncertain systematic position.

3. In *Synechococcus* and *Dunaliella*, the heptadecenes are accompanied by smaller amounts of di-, tri- and tetraolefins.

4. The highly unsaturated 3,6,9,12,15,18-heneicosahexaene (HEH) predominates in the Bacillariophyceae, Dinophyceae, Cryptophyceae, Haptophyceae and Euglenophyceae. In other classes this hydrocarbon is absent.

5. *Rhizosolenia setigera* contains n-heneicosane, presumably derived from HEH by hydrogenation.

A corresponding tetraolefin is a minor component of *Thalassiosira fluviatilis*.

6. Limited observations suggest that HEH is most effectively synthesized during the logarithmic growth phase; in cultures harvested during the stationary phase, more highly saturated hydrocarbons in the C_{14} to C_{17} range become more abundant.

7. The caution expressed by GELPI et al. (1970) against premature correlation of hydrocarbon chemistry with evolutionary position is well founded, some earlier generalizations appear no longer valid.

8. Algae are characterized by the presence of relatively few hydrocarbons, mostly straight chain alkanes and alkenes and some monomethylalkanes. Pristane is present, but at a low concentration. Zooplankton, on the other hand, contains the complex assemblage of C_{19} and C_{20} isoprenoid alkanes and alkenes which are derived from phytol. The hydrocarbon composition of ancient sediments and of petroleum is far more complex; many isomeric compounds belonging to different homologous series are found, olefins are absent, and alicyclic and aromatic compounds occur at much higher concentrations than in living organisms.

9. Hydrocarbon analysis may be a tool for the detection of algal species in mixed plankton or in mixed algal lipids ingested by certain herbivores. Also, detailed hydrocarbon analysis enables the distinction between hydrocarbons of recent biogenic origin and hydrocarbon pollutants from fossil fuels.

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