Isolation of Heneicosa-1,6,9,12,15,18-hexaene and -1,6,9,12,15-pentaene from the Alga *Fucus vesiculosus*

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Summary The non-saponifiable lipid fraction from the marine brown alga *Fucus vesiculosus* has been shown to contain two new polyolefins, heneicosa-1,6,9,12,15-pentaene and -1,6,9,12,15,18-hexaene as well as n-alkan-1-ols, n-paraffins, squalene, and β-carotene.

DURING an investigation of the constituents of the marine brown alga *Fucus vesiculosus* two new C_{21} polyolefins have been isolated as odourless, colourless oils by chromatography (25% silver nitrate–silica gel; ether–light petroleum) of the hydrocarbon portion of the non-saponifiable fraction of the light petroleum extract from fresh dried material which was harvested in mid-February. The oils easily oxidised in air to give the characteristic sea-weed odour. Before analytical data were obtained the polyolefins were purified by p.l.c. and examined within 2 h.

$MeCH_2{\cdot}CH{=}CH{\cdot}[CH_2{\cdot}CH{=}CH]_4{\cdot}[CH_2]_3{\cdot}CH{=}CH_2$ (I)

$Me{\cdot}[CH_2{\cdot}CH{=}CH]_5{\cdot}[CH_2]_4{\cdot}Me$ (II)

$Me{\cdot}[CH_2]_3{\cdot}[CH_2{\cdot}CH{=}CH]_4{\cdot}[CH_2]_3{\cdot}CH{=}CH_2$ (III)

The more abundant polyolefin (I) was a hexaene $C_{21}H_{32}$ (*M m/e* 284). Its u.v. spectrum (C_6H_{14}) showed only end absorption indicating the absence of conjugation. I.r. bands at 920, 1000, and 1640 cm^{-1} and 720 and 1650 cm^{-1} indicated $-CH{=}CH_2$ and *cis*-disubstituted double bonds respectively. Its n.m.r. spectrum (CCl_4) was similar to that of methylene-interrupted polyunsaturated fatty acids;[1] τ 4·39 (1H, m, $CH_2{=}C\mathit{H}$–), 4·72 (10H, m, $-C\mathit{H}{=}C\mathit{H}-$), 5·07 (2H, m, $C\mathit{H}_2{=}CH$–), 7·19 (8H, m, $=CH{-}C\mathit{H}_2{-}CH=$), 7·94 (6H, m, $-C\mathit{H}_2{-}CH=$), 8·53 (2H, q, *J* 7 Hz, $=CH{-}CH_2{\cdot}C\mathit{H}_2{\cdot}CH_2{\cdot}CH=$), and 9·04 (3H, t, *J* 7·5 Hz, $\mathit{Me}CH_2{-}CH=$).

The hexaene was hydrogenated with Pd–C to give heneicosane. Ozonolysis with reductive work-up gave propanal proving the presence of $MeCH_2{\cdot}CH=$. These results suggested that the hexaene was *cis,cis,cis,cis,cis*-heneicosa-1,6,9,12,15,18-hexaene (I), the less likely alternative structures having the $-[CH_2]_3-$ grouping at other positions in the carbon chain. The position of this grouping was confirmed by the partial hydrogenation of the hexaene with bis(triphenylphosphine)dichlororuthenium[2] which causes preferential hydrogenation of terminal double bonds. A 51% yield of the dihydro-compound (II) was obtained (*m/e* 286, no absorption at τ 4·4 and 5·1 or ν_{max} 920, 1000, and 1640 cm^{-1}). A weak band at 975 cm^{-1} indicated that (II) may have contained some *trans*-isomers formed during hydrogenation. Ozonolysis of (II) followed by reductive cleavage afforded propanal and hexanal. Compound (II) was methoxylated by methoxymercuration.[3]

The mass spectrum of the product had four major peaks; *m/e* 159 (63%) and 145 (21%) confirming the presence of $MeCH_2{\cdot}CH{=}CH{-}CH_2{-}CH{=}CH-$ and at 129 (50%) and 152 (28%) confirming the presence of $Me{\cdot}[CH_2]_4{\cdot}CH{=}CH$. Methoxylation of the hexaene (I) gave a product which afforded major peaks at *m/e* 159 (95%) and 145 (17%) which can arise from both ends of (I).

The less abundant polyolefin (III) was a pentaene $C_{21}H_{34}$ (*M m/e* 286); $\nu_{max.}$ 2970, 1650(sh), 1640, 1000, 920, and 720 cm^{-1}; τ 4·35 (1H, m, $CH_2{=}C\mathit{H}$–), 4·68 (8H, m, $-C\mathit{H}{=}C\mathit{H}-$), 5·03 (2H, *m*, $C\mathit{H}_2{=}CH$–), 7·21 (6H, m, $=CH{-}C\mathit{H}_2{-}CH=$), 7·93 (6H, m, $-CH_2{-}CH=$), 8·66 (8H, m, $-CH_2$), and 9·09 (3H, distorted t, $MeCH_2{\cdot}$). These results suggested that the polyolefin was *cis,cis,cis,cis*-heneicosa-1,6,9,12,15-pentaene (III). This was confirmed by its partial synthesis. Eicosa-5,8,11,14-tetrayn-1-oic acid was converted into eicosa-5,8,11,14-tetraenyl bromide by reduction to the alcohol, hydrogenation with Lindlar's catalyst to the predominantly *cis*-orientated polyene alcohol, and bromination with triphenylphosphine dibromide. The bromide was converted into its Wittig salt which was treated with base and then paraformaldehyde. Best results were obtained with n-butyl-lithium in dimethylformamide, when the product was shown by g.l.c. to be 90% (III) together with small amounts of conjugated material.

The two olefinic hydrocarbons may arise from the corresponding C_{22} polyunsaturated acids, although these have not been found[4] in *F. vesiculosus* and when found in marine algae are in low concentration. In contrast *F. vesiculosus* does contain[4] the 20:4 and 20:5 polyunsaturated acids to the extent of 10·1 and 7·6% of the total fatty acid content.

In addition to these two hydrocarbons, fucosterol[5] and phytol,[6] a series of n-alkan-1-ols between C_{11} and C_{16}, a series of n-paraffins between C_{10}–C_{35}, phytane, pristane, squalene, and β-carotene were shown to be present in the alga. The paraffin distribution showed no odd–even preference, with a maximum at C_{15}, and a secondary maximum at C_{27} and a minimum at C_{19}. The distribution is typical of that found by Clark and Blumer[7] for other species of brown algae.

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