

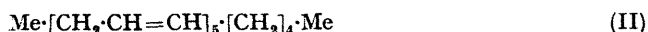
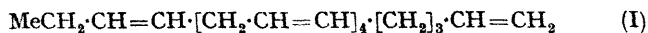
## Isolation of Heneicosa-1,6,9,12,15,18-hexaene and -1,6,9,12,15-pentaene from the Alga *Fucus vesiculosus*

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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  $\beta$ -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.



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  $\text{cm}^{-1}$  and 720 and 1650  $\text{cm}^{-1}$  indicated  $-\text{CH}=\text{CH}_2$  and *cis*-disubstituted double bonds respectively. Its n.m.r. spectrum ( $\text{CCl}_4$ ) was similar to that of methylene-interrupted polyunsaturated fatty acids;<sup>1</sup>  $\tau$  4.39 (1H, m,  $\text{CH}_2=\text{CH}-$ ), 4.72 (10H, m,  $-\text{CH}=\text{CH}-$ ), 5.07 (2H, m,  $\text{CH}_2=\text{CH}-$ ), 7.19 (8H, m,  $=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ ), 7.94 (6H, m,  $-\text{CH}_2-\text{CH}=\text{CH}-$ ), 8.53 (2H, q,  $J$  7 Hz,  $=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$ ), and 9.04 (3H, t,  $J$  7.5 Hz,  $\text{MeCH}_2-\text{CH}=\text{CH}-$ ).

The hexaene was hydrogenated with Pd-C to give

heneicosane. Ozonolysis with reductive work-up gave propanal proving the presence of  $\text{MeCH}_2-\text{CH}=\text{CH}-$ . 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  $-\text{[CH}_2\text{]}_3-$  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<sup>2</sup> which causes preferential hydrogenation of terminal double bonds. A 51% yield of the dihydro-compound (II) was obtained ( $m/e$  286, no absorption at  $\tau$  4.4 and 5.1 or  $\nu_{\text{max}}$  920, 1000, and 1640  $\text{cm}^{-1}$ ). A weak band at 975  $\text{cm}^{-1}$  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.<sup>3</sup>

The mass spectrum of the product had four major peaks;  $m/e$  159 (63%) and 145 (21%) confirming the presence of  $\text{MeCH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$  and at 129 (50%) and 152 (28%) confirming the presence of  $\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CH}=\text{CH}$ . 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);  $\nu_{\text{max}}$  2970, 1650(sh), 1640, 1000, 920, and 720  $\text{cm}^{-1}$ ;  $\tau$  4.35 (1H, m,  $\text{CH}_2=\text{CH}-$ ), 4.68 (8H, m,  $-\text{CH}=\text{CH}-$ ), 5.03 (2H, m,  $\text{CH}_2=\text{CH}-$ ), 7.21 (6H, m,  $=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ ), 7.93 (6H, m,  $-\text{CH}_2-\text{CH}=\text{CH}-$ ), 8.66 (8H, m,  $-\text{CH}_2-$ ), and 9.09 (3H, distorted t,  $\text{MeCH}_2$ ). 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-tetraenyl bromide was converted into eicosa-5,8,11,14-tetraenyl alcohol 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<sup>4</sup> in *F. vesiculosus* and when found in marine algae are in low concentration. In contrast *F. vesiculosus* does contain<sup>4</sup> 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<sup>5</sup> and phytol,<sup>6</sup> 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  $\beta$ -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<sup>7</sup> for other species of brown algae.

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