Short Paper

Hydrocarbons of a Chiton*1

Previously, the hydrocarbons of sea urchins, *Temnopleurus toreumaticus* and *Anthocidaris crassispina*, were examined by the authors.¹⁾ As to the hydrocarbons of mollusks, the predominance of *n*-heptadecane, *n*-heneicosane and *n*-heneicosahexaene in the scallop, *Aequipecten irradians*, and oyster, *Crassostrea virginica*, were indicated by BLUMER *et al.*,²⁾ and pristane, *n*-eicosene and *n*-heneicosahexaene in the mussel, *Mytilus edulis*, by LEE *et al.*³⁾ This paper deals with the hydrocarbons of a mollusk (Polyplacophora), chiton, *Liolophura japonica*. They are herbivorous and feed on algae that they scrape from the surface of rocks.

Isolation and analyses of the hydrocarbons were carried out as described previously.¹⁾ Hydrocarbons (0.007% of the muscle) were separated into three fractions by using silver nitrate-impregnated thin-layer chromatography with 2% benzene-hexane as solvent: saturated (30%), unsaturated (38%) and highly unsaturated (32%) hydrocarbons.

Gas-liquid chromatography (GLC) of the alkanes on Apiezon L and FFAP indicated the predominance of *n*-heptadecane (31% of the alkanes). However, the carbon preference index (CPI)*2 of *n*-alkanes calculated over the range C₂₀ to C₃₃ was 0.6, and there was a slight even-carbon predominance.

GLC of the alkene fraction showed two major peaks of KOVATS' retention indices of 1498 and 1688 on Apiezon L, and 1558 and 1745 on FFAP, respectively. The data indicate that the alkenes were monoenes of C₁₅ and C₁₇. The infrared absorption spectrum showed the bands at 714 cm⁻¹ (*cis*-olefin) and at 913 cm⁻¹ (vinyl). The alkene fraction was oxidized with OsO₄ in pyridine-dioxane, and resulted diol was condensed with acetone. The *O*-isopropylidene derivative of alkene diol was subjected to GLC/mass spectrometry. GLC on OV-1 indicated that the derivative contained four components (1, 6.9%; 2, 16.9%; 3, 29.8%; 4, 46.5%). The mass spectra of *O*-isopropylidene derivatives of alkenes give the ions (x and y) arising from α -cleavage of the dioxolane ring. In cases in which the dioxolane ring has the position closer to the terminal position, another ion (z) indicate the position of the ring.⁴⁾

The GLC/mass spectra gave an intense peak conceived to be an ion due to loss of a methyl group from the dioxolane ring (M⁺-15), at m/e 269 (component 1, 2, and 3), or 297 (component 4). Moreover, the spectra gave the ion z at m/e 100 (component 1), m/e 86 (component 2), m/e 72 (component 3), or ions x and y at m/e 157 and 255 (component 4). The other peaks were interpreted as follows: m/e 43 (C₃H₇⁺, 100%) and 59 (C₃H₇O⁺) in the spectra of every components, 227 (M⁺-CH₃-C₂H₅O) (component 1, 2, and 3), or 255 (M⁺-CH₃-C₂H₅O and y) (component 4). On the basis of the above data, the alkenes of the chiton were identified as *cis*-3-, *cis*-2-, and 1-pentadecene and *cis*-5-heptadecene. Furthermore, highly unsaturated hydrocarbon was identified as squalene by GLC on Apiezon L and FFAP.

In the case of the sea urchin, *T. toreumaticus*, the authors¹⁾ have indicated that the alkene was composed of largely *cis*-7-heptadecene. BLUMER *et al.*⁵⁾ have indicated that 5-heptadecene was the principal hydrocarbon of blue-green algae (Cyanophyceae), *Synechococcus bacillaris*, and pentadecene was the major constituent of a yellow-green algae (Xanthophyceae), *Tribonema aequale*, though the position of the double bond was unknown.

The chitons were collected on the coast of Ninoshima Island in Hiroshima Bay. The unresolved peak envelope of gas chromatogram of the *n*-alkanes, CPI₁₄₋₂₀ (1.7), and *n*-C₁₈ ratio (12.4) suggested that the animals were polluted by low levels of oil.*2 However, the presence of considerable amounts of alkenes and squalene indicated that the major part of the hydrocarbons are biogenetic.

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*1 ヒザラガイの炭化水素 (保田茂次郎・深宮齊彦: 広島大学総合科学部).

*2 R. C. CLARK, Jr. and J. S. FINLEY: Proceedings of the 1973 Joint Conference on Prevention and Control of Oil Spills. API/EPA/USCG, Washington, 1973, pp. 161-172.