Studies on Steroids. XXXIX.1) Sterol Profiles of Red Algae. (2)2)

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Five species of red algae were examined for sterols. Desmosterol was identified in Porphyra tenera, Pilota pectinata and Rhodymenia palmata and the last algae was found to contain lioagosterol (I) and cholesta-5,25-dien-3β,23-diol (II)

In the previous report,3) we have described the sterol components in twelve different species of red algae belonging to orders Gelidiales, Cryptonemiales and Gigartinales. In that investigations a variety of 5,6-dihydrosterol (stanol) in which cholestanol was the major one, was identified in four species. Another noteworthy was that desmosterol was not detected in any of these twelve species although this sterol has appeared to be widely distributed in red algae.4) Desmosterol may be a suitable starting compound for synthesis of biologically active steroids, e.g., active forms of vitamin D3.5) Now we have extended the search for sterols to orders Bangiales (1 species) and Rhodymeniales (4 species).

In the same manner as described previously,3) sterols in unsaponifiable fractions of algae were analyzed as their trimethylsilyl ethers by means of gas chromatograph–mass spectrometry (GC–MS) technique. Table 1 shows the estimations of cholesterol and desmosterol contents in the algae. GC patterns of Odonthalia corymbifera and Laurencia nipponica were extremely simple, indicating cholesterol almost the sole sterol in these species. Porphyra tenera (commercial Nori) contained desmosterol in addition to cholesterol. The other two algae, i.e., Pilota pectinata and Rhodymenia palmata (dulse) showed complex sterol profiles. Besides cholesterol and desmosterol the following sterols were detected in P. pectinata: 24-dimethylchola-5,22-dien-3β-ol, 24-methylene cholesterol and isofucosterol. R. palmata may be one of the most extensively studied algae on sterol components, and desmosterol has been reported as the

| Table 1. Amounts of Cholesterol and Desmosterol in Algae a) |
| Algae                               | Cholesterol (%) | Desmosterol (%) |
| Bangiales                           |                |                 |
| Porphyra tenera Kjellman (Asakusa-nori) | 0.006         | 0.002          |
| Rhodymeniales                       |                |                 |
| Odonthalia corymbifera J. Agardh (Hakasenokogirihiba) | 0.004         | —              |
| Laurencia nipponica (Uraso)         | 0.18           | —              |
| Pilota pectinata Kjellman (Kushibenihiba) | 0.01         | 0.003          |
| Rhodymenia palmata Greville (Daru)  | 0.001          | 0.003          |

a) Estimated gas chromatographically and expressed in % concentrations based on dry weight of algae.

3) Location: Ookayama, Meguro-ku, Tokyo, 152, Japan.
major one in British, Canadian and French dulse. In accordance with these previous findings, R. palmata presently harvested in the sea near to Hokkaido, Japan has also been found to contain this sterol as the principal one. GC-MS analysis (Fig. 1) indicated the coexistence of 22-dehydrocholesterol, cholesterol and 24-methylcholesterol.

The broad peak at retention time of 22.5 min has been revealed to be consisted of three sterols when analyzed by GC equipped with a glass capillary column coated with OV-17 or OV-101. By mass chromatographic studies of this portion (Fig. 2), these sterols were identified as isofucosterol, liagosterol (I) and its isomer (II). The structure of the latter two sterols were further confirmed by the complete agreement of retention time on GC and mass spectra with those of authentic samples.

Liangosterol (I) has recently been isolated from Liagora distenta and Scinaia furcellata belonging to the order Nemaliales and has been proposed to be confined to plant of this order. Cholesta-5,25-diene-3β,25-diol (II) may be to our knowledge a new sterol to algae. The cooccurrence of these sterols (I and II) with desmosterol

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in *R. palmata* seems to suggest that I and II might be biosynthesized from desmosterol *via* photosensitized oxygenation or related mechanism. However, the possibility that these diols (I and II) would be artifact produced from desmosterol during air-drying of algae or extraction/isolation procedures, should be also considered.

**Experimental**

The algae were harvested at Muroran bay, Hokkaido, Japan, and identified by Profs. T. Nakamura and M. Tatewaki, Hokkaido University. Extraction of sterols and the analysis of their trimethylsilyl ethers by GC-MS were carried out as previously described. Mass chromatography was performed with Shimadzu-LKB 9000 Gas Chromatograph-Mass Spectrometer equipped with GC-MASS PAC-300 DG data processing system; OKITAC-4300C minicomputer with 12K core, a typewritten digital plotter, a magnetic disk and an interface. For details see Fig. 2 legend.

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**Studies on the Synthesis of Cardiotonic Steroids. II.** Synthesis of 17β-(3-Furyl)-5β,14β-androstane-3β,14β-diol

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17β-(3-Furyl)-5β,14β-androstane-3β,14β-diol, a promising relay compound leading to digitoxigenin, was synthesized starting with 3β-acetoxy-5β-pregn-14-en-20-one.

Our continuous interest in the exploration of new synthetic routes to naturally occurring cardenolide led us to establish the effective synthetic method of the title compound, since the compound is known to be convertible to digitoxigenin. The starting material employed for this objective was 3β-acetoxy-5β-pregn-14-en-20-one (I) that proved the attractive intermediate in our previous digitoxigenin synthesis. Derivation of furan ring from the side chain of I and subsequent formation of 14β-hydroxy group have completed the present approach as described below.

2) Location: Gojuku, Toyama, 930, Japan.