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Structure of Sargatriol, a New Isoprenoid Chromenol from a Marine Alga: *Sargassum tortile*

The ether extract of *Sargassum tortile*, a marine alga, was examined and a new isoprenoid chromenol was isolated.

The structure of this compound was determined to be Ia on the basis of the chemical and spectroscopic evidence.

Sargassum tortile, a brown alga, has been known to contain antitumor substances in its water-soluble fraction[1] and several substances which stimulate the settling of swimming larvae to this plant in the benzene-soluble fraction.[2] From a biologically active fraction obtained by chromatographic separation of the latter, δ-tocotrienol (II) and its epoxide have been characterized.[2] Recently we isolated a new phenolic compound, designated as sargatriol, from the ether extract of this alga and determined the structure to be Ia.

Sargatriol (Ia), pale yellow oil, $[\alpha]_D +16°$ ($CHCl_3$), revealed the molecular ion peak at *m/e* 426 ($C_{27}H_{38}O_4$) in the mass spectrum[3] and a strong hydroxyl band in the infrared (IR) spectrum.[3] Its ultraviolet (UV) spectrum[3] exhibited an absorption maximum at 335 nm (ε 2560) which shifted to 355 nm on addition of ethanolic KOH, indicating the presence of a phenolic styrene chromophore. The nuclear magnetic resonance (NMR) spectrum[3] showed signals at δ 1.33 (3H, *tert*-CH_3), 1.58, 1.65 (each 6H, four vinyl CH_3), 2.10 (3H, toluene CH_3), 3.80 (1H, d, J=8 Hz, C$\underline{H}$OH), 4.30 (1H, t, J=8.5 Hz, C$\underline{H}$OH), 5.53, 6.25 (each 1H, pair of d, J=10 Hz, olefinic H), 4.9—5.6 (3H, olefinic H), 6.32, and 6.48 (each 1H, pair of d, J=2.5 Hz, aromatic H).

Acetylation of Ia with acetic anhydride–pyridine gave an oily acetate (Ib), $[\alpha]_D +34°$ ($CHCl_3$), $C_{33}H_{44}O_7$ (high-resolution mass spectrum,[3] M^+ Calcd.: 552.3087; Found: 552.3092), UV λ_{max} 320 nm (ε 3310). The IR spectrum of Ib showed strong absorptions at 1735 and 1235 cm^{-1} and the NMR spectrum (Fig. 1) demonstrated signals of newly introduced three acetyl groups at δ 2.24 (phenol acetate), 1.99, and 2.03 (carbinol acetates) and of two hydrogens geminal to the acetoxyl groups at δ 5.18 (d, J=8 Hz) and 5.72 (q, J=8, 9.5 Hz) along with other signals.

As illustrated in Fig. 1, nuclear magnetic double resonance (NMDR) experiments between the signals at δ 5.72 (C$\underline{H}$OAc) and 5.18 (C$\underline{H}$OAc) and 5.05 (olefinic H) demonstrated their coupling relationship, and moreover a 12% nuclear Overhauser effect (NOE) increase in the signal at δ 5.18 was noticed by irradiation of a triplet at δ 5.50 attributable to an olefinic proton. On the other hand, decoupling experiments between the signals at δ 6.67 and 6.54 and between those at δ 6.26 and 5.52 revealed that these are ascribed to aromatic *meta* hydrogens and *cis*-orienting olefinic hydrogens, respectively. Furthermore, irradiation at δ 6.54 gave an 8% NOE increase in the signal intensity at δ 6.26 and also irradiation of the toluene

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1) S. Nakazawa, H. Ohno, M. Ohtsuki, T. Izawa, H. Kuroda, M. Ishiyama, K. Ochiai, H. Kawabe, I. Umezaki, and Y. Yoneda, Abstracts of Papers, The 91st Annual Meeting of Pharmaceutical Society of Japan, Fukuoka, March, 1971, p. 252.

2) A.S. Kumanireng, T. Kato, and Y. Kitahara, Symposium Papers, The 17th Symposium on the Chemistry of Natural Products, Tokyo, 1973, p. 94.

3) Mass spectra and high-resolution mass spectra were determined on a Hitachi Mass Spectrometer RMU-6D using a direct inlet system (MG-150) and on a JMS-01SG Double-Focusing Mass Spectrometer, respectively. IR and UV spectra were taken in $CHCl_3$ and EtOH, respectively, and NMR spectra were measured in $CDCl_3$ on a Varian A-60 or HA-100D Spectrometer. GC-MS was carried out on a Hitachi Mass Spectrometer RMU-6E combined with a Hitachi Gas Chromatograph Model K-53 using a 10% polyethylene glycol 20M column.

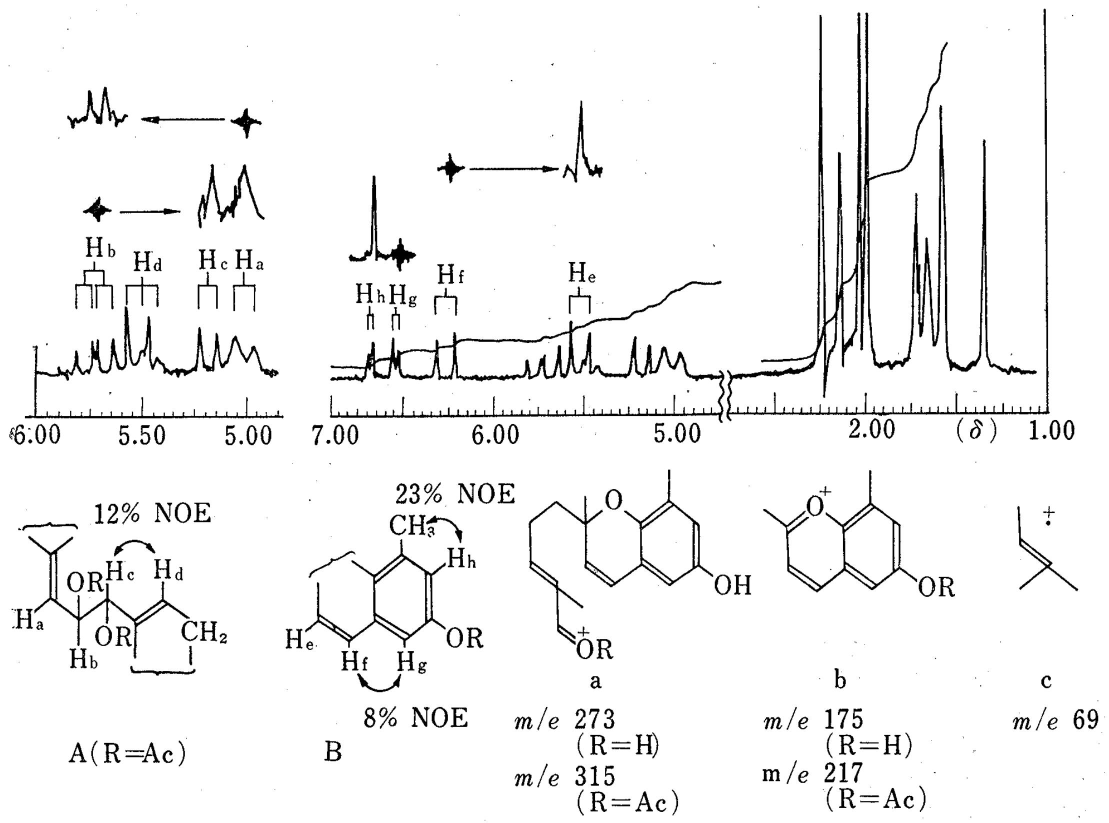

Fig. 1. NMR and NMDR Spectra of Sargatriol Acetate (Ib) (100 MHz)

methyl signal at δ 2.14 gave a 23% NOE increase in the signal at δ 6.67. From these observations, presence of the partial structures A and B could be postulated in Ib.

Meanwhile, the gross structure of sargatriol (Ia) was inferred by its mass spectrum which showed three intense peaks at *m/e* 273, 175 (base peak), and 69. In the mass spectrum of its acetate (Ib), the corresponding peaks were observed at *m/e* 315, 217 (base peak), and 69, whose compositions were found to be $C_{19}H_{23}O_4$ (Calcd.: 315.1596; Found: 315.1615), $C_{13}H_{13}O_3$ (Calcd.: 217.0865; Found: 217.0893), and C_5H_9 (Calcd.: 69.0704; Found: 69.0705), respectively, by the high-resolution mass spectrum. As a consequence, these peaks may be ascribed to the fragment ions a̲, b̲, and c̲, respectively.[2)]

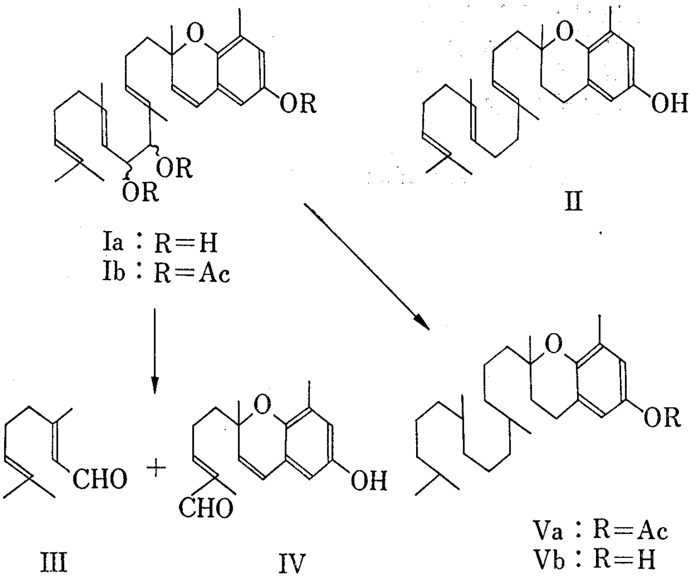

Chart 1

Then the periodide oxidation of Ia was undertaken, where two conjugated aldehydes were obtained after preparative thin-layer chromatography. The less polar product, colorless oil, showed an IR band at 1665 cm^{-1} and NMR signals at δ 10.10 (1H, d, J=8 Hz, CH̲O), 5.90 (1H, broad d, J=8 Hz, olefinic H), 5.10 (1H, m, olefinic H), 2.17 (3H, d, J=1.5 Hz, vinyl CH_3), 1.70, and 1.62 (each 3H, broad s, two vinyl CH_3). Its mass spectrum revealed the M$^+$ peak at m/e 152 ($C_{10}H_{16}O$) together with strong peaks at m/e 94, 84, 69, and 41 (base peak). Eventually, this compound was proved to be identical with citral-a (III)[4] by direct GC-MS comparison[3] with an authentic sample. On the other hand, though the more polar product was unstable and could not be isolated in pure state, it showed an IR band at 1670 cm^{-1} and an NMR signal for an aldehyde proton at δ 9.42 (s). The mass spectrum gave the molecular ion peak at m/e 272 ($C_{17}H_{20}O_3$) and the base peak at m/e 175 (b). From these spectral data, this compound would be assigned to the structure IV.

Summarizing the foregoing findings, the structure of sargatriol might be represented by the formula Ia. This was further confirmed by catalytic hydrogenation of Ib over Pd-C, which caused the hydrogenolysis of two acetoxyl groups concomitant with the hydrogenation of double bonds, giving a saturated phenol acetate (Va), $C_{29}H_{48}O_3$ (M$^+$ Calcd.: 444.3603; Found: 444.3554). Hydrolysis of the latter (Va) gave an oily phenol (Vb), whose IR and NMR spectra were identical with those of the hexahydro compound (Vb)[5] of δ-tocotrienol (II).

Thus the structure of sargatriol is unambiguously assigned to the formula Ia except the stereochemistry which is currently under investigation. Examination of the biological activity of this compound is also in progress.

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5) We are indebted to Prof. Kitahara of Tohoku University for the sample of Vb.