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The Structure of Tedanin, a New Carotenoid of *Tedania digitata* (O. Schmidt)

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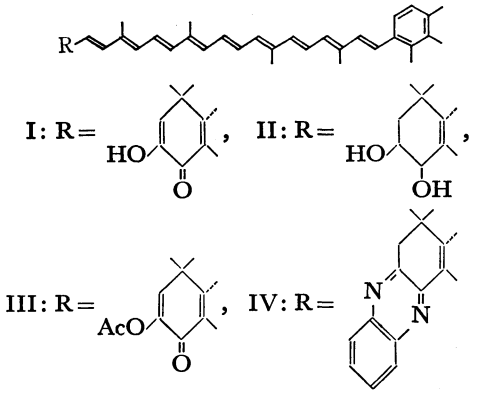
Synopsis. A new carotenoid, tedanin, which was isolated as a main pigment from a sea sponge, "*Tedania digitata* (O. Schmidt)," was shown to have the (I) structure by means of spectroscopic and chemical evidence.

The carotenoids of sponges have been the subject of many investigations;[1] for instance, a novel class of carotenoids with aromatic end-groups has been discovered.[2] However, the pigments of one sea sponge, "*Tedania digitata* (O. Schmidt)," have not so far been reported. This paper will describe the isolation of a new carotenoid named tedanin from the sponge and structural studies which showed that the pigment has the structure represented by Formula (I).



Results and Discussion

Tedanin crystallizes in the form of purplish-black prisms with a mp of 188—190 °C. The molecular formula, $C_{40}H_{48}O_2$, was established by high-resolution mass spectrometry and by elemental analysis. The UV spectrum shows a single round absorption at 490 nm in benzene and one at 500 nm in pyridine, as is shown in Fig. 1. The location and the curve of the

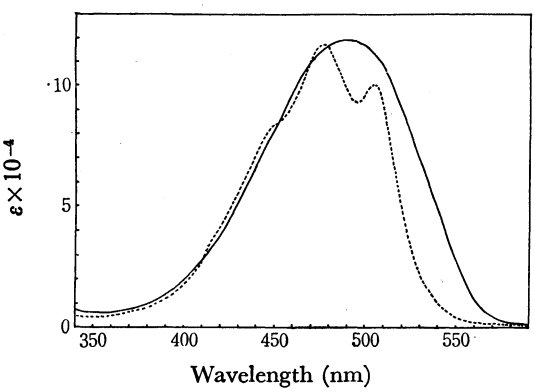


Fig. 1. Absorption spectra of tedanin (I) (——) and tetrahydrotedanin (II) (----) (benzene)

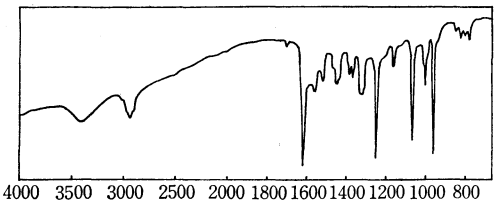


Fig. 2. IR Spectrum of tedanin (I) (KBr disk).

absorption are very similar to those of astacene.[3] Other properties, such as chromatographic behaviour, solubility, and solvent partition, also resembled those of astacene.[3] These facts seem to indicate the structural similarity of these two pigments. The IR spectrum of this pigment is shown in Fig. 2. The occurrence of peaks at 1620, 1250, 1060, 1380, and 1365 cm^{-1}, which are also present in the spectrum of astacene[4] suggests the presence of a diosphenol grouping. In addition to the ion peaks characteristic of the polyene chain of typical carotenoids [*m/e* 560(M), 468(M—92), 454(M—106), 106, and 91],[5] the mass spectrum of the pigment gives peaks at *m/e* 408(M—152), 203, 152, and 137, which are also considered to be evidence for the presence of a diosphenol end-group.[6] Furthermore, a diagnostically important peak was observed at *m/e* 133; this clearly indicates the presence of a trimethylphenyl end-group.[7] Further evidence of the presence of these end-groups was obtained from the NMR spectral study. The signals at δ 1.32(6H) and 2.11(3H) can be assigned to the 1,1-dimethyl and 5-methyl protons of the diosphenol group respectively.[8] The signals appearing at the lower field [δ 2.22(3H) and 2.31(6H)] are considered to arise from the three methyl groups attached to the aromatic nucleus, and a comparison of the chemical shifts with those of three aryl methyl groups of okenone[9] and 4′-desoxo-okenone[10] suggests that the second end-group is 2,3,4-trimethylphenyl. This was confirmed by the presence of the double doublet signal centered at δ 6.97(1H) and δ 7.27(1H) (J=7.2 Hz), which is characteristic of aromatic protons at the 5- and 6-positions of this end-group.[1c] The IR absorption at 800 cm^{-1} attributable to two adjacent aryl hydrogens is in agreement with this conclusion.

From the above evidence, the structure of tedanin can be formulated as is shown in Formula (I). The all-*trans* configuration of I was based on the absence of the *cis*-peak in the UV spectrum[11] and the presence of a sharp singlet at 960 cm^{-1} in the IR spectrum.[12]

Further evidence supporting the (I) structure comes from chemical studies. The reduction of tedanin with sodium borohydride resulted in a hypsochromic shift, accompanied by the new formation of fine structures

in the UV spectrum (Fig. 1). This is in accordance with the formation of a tetrahydro compound (II). The UV spectral data of II [λ_{max}, 496 nm (CS_2)] are very similar to those of β-renierapurpurin [λ_{max}, 497 nm (CS_2)][13] but differ from those of β-isorenieratene [λ_{max}, 487 nm (CS_2)].[13] This apparently shows that the chromophore of this reduction product (II) is not of the β,φ-carotene-type but of the β,χ-carotene-type. The acetylation of tedanin with acetic anhydride and pyridine afforded an acetate (III). Finally, the quinoxaline derivative (IV) was prepared by a reaction with *o*-phenylenediamine. The structures of these derivatives were confirmed by the fact that the mass spectra of these derivatives showed the expected molecular ion and a regular pattern of fragmentations.[14] These facts strongly support the conclusion that the structure of tedanin is 3-hydroxy-2,3-didehydro-β,χ-carotene-4-one (I).

However, it is not clear whether tedanin originally occurs in the sponge or whether it is an artifact formed by the oxidation of a ketol compound.

Experimental

All the melting points are uncorrected. The solutions were concentrated under reduced pressure below 45 °C under nitrogen. The instruments used for the measurements of the spectra were as follows. UV spectra; Hitachi, Model EPS-3T. IR spectra; Hitachi, Model 215. NMR spectra; Hitachi, Model R-22. Mass spectra; Hitachi, Model RMU-4 and JEOL, Model JMS-01SG.

Isolation of Tedanin (I). Specimens of the sponge, (80 g, dry weight), collected at Amakusa in Kumamoto Prefecture in November, 1972, were repeatedly extracted with acetone, and the pigments were transferred into benzene by the addition of water. After the evaporation of the solvent, the pigments were saponified with 10% methanolic potassium hydroxide in petroleum benzine at room temperature for 12 hr and then separated into epiphasic and hypophasic fractions by repeated partitioning between 90% methanol and petroleum benzine. The hypophasic methanol solution was then diluted with water, and the pigments were extracted again with benzene. The evaporation residue was treated with acetone, and the insoluble colorless impurities were removed repeatedly as completely as possible. The residue was finally diluted with a small quantity of petroleum benzine and left to stand in an ice-box. Repeated recrystallizations of the precipitate from methylene chloride–ethanol gave tedanin (I, 5 mg) as purplish-black prisms; mp 188—190 °C. Found: C, 85.20; H, 8.56%. Calcd for $C_{40}H_{48}O_2$: C, 85.66; H, 8.63%. UV spectra: λ_{max}, 490 nm ($\varepsilon=1.19\times10^5$)($C_6H_6$); 500 nm (pyridine). IR spectrum; Fig. 2. NMR spectrum: δ ($CDCl_3$) 1.32 (6H, s, 1,1-dimethyl); 2.00 and 2.03 (each 6H, s, chain methyl); 2.11 (3H, s, 5-methyl); 2.22 and 2.31 (3H, and 6H, respectively, s, arylmethyl); 6.03—6.90 (15H, m, olefinic protons); 6.97 and 7.27 (2H, dd($J=7.2$ Hz), aromatic protons). Mass spectrum: 560.3579 (M. Calcd for $C_{40}H_{48}O_2$, 560.3655), 408(M−92), 454 (M−106), 408(M−152), 203, 152, 137, 133, 106, 105, 92, 91, 77, 44, 28, 18.

Reduction of Tedanin to Tetrahydrotedanin (II). Tedanin (I, 1 mg) dissolved in ethanol (10 ml) was treated with sodium borohydride (40 mg) for 1 hr at room temperature. The mixture was diluted with water and extracted with benzene. The extract was washed with dilute hydrochloric acid, an aqueous sodium bicarbonate solution, and then water, dried, and evaporated. Recrystallizations of the residue from methylene chloride–ethanol gave II as red prisms (0.6 mg); mp 186 °C. UV spectra: λ_{max}, 446_{sh}, 475 ($\varepsilon=1.17\times10^5$), 506 nm ($C_6H_6$); 453_{sh}, 496, 524 nm (CS_2). Mass spectrum; 564 (M), 546, 528 472, 458, 440, 422, 408 395, 348, 329, 289, 249, 221, 133, 106, 105, 92, 91, 77, 44, 28, 18.

Acetylation of Tedanin to Tedanin Acetate (III). To a solution of tedanin (I, 1 mg) in dry pyridine (10 ml), was added acetic anhydride (1 ml). The reaction mixture was then left to stand at room temperature for 6 hr and extracted with benzene. The treatment of the extract by the usual procedure gave III as black prisms (0.65 mg); mp 172—173 °C. UV spectrum: λ_{max}, 487 nm ($\varepsilon=1.28\times10^5$)($C_6H_6$). Mass spectrum: 602 (M), 560, 510, 496, 454, 404, 362, 347, 329, 289, 133, 106, 105, 92, 91, 77, 51, 44, 28.

Preparation of Quinoxaline Derivative (IV). To a solution of tedanin (I, 1.8 mg) in glacial acetic acid (1 ml), was added *o*-phenylenediamine (15 mg). The mixture was kept at 100 °C on a water bath for 2 hr and then extracted with benzene. The treatment of the extract by the usual procedure gave IV as reddish-purple crystals (0.3 mg); mp 150—151 °C. UV spectrum: λ_{max}, 493 nm ($\varepsilon=1.16\times10^5$)($C_6H_6$). Mass spectrum: 632 (M), 617, 540, 526, 511, 434, 419, 393, 355, 343, 329, 289, 277, 275, 259, 249, 133, 105, 91, 77, 55, 41.

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