BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1884—1885 (1973)

Two Natural Acetylenic Aromatic Carotenoids

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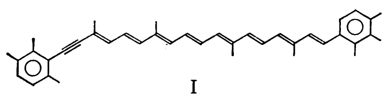
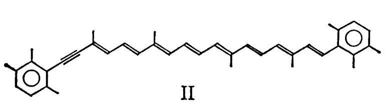
(Received July 6, 1972)

Among seven carotenoid hydrocarbons[1] isolated from a sea-sponge "*Reniera japonica*," five major pigments, α-carotene,[1] β-carotene,[1] renieratene,[2] isorenieratene,[3] and renierapurpurin,[4] have been identified or structurally elucidated. Two other minor pigments (mp 205 and 194 °C) have remained structurally unsolved because of the paucity of materials. Recently, a considerable amount of the samples has been isolated, and, as will be shown below, enough evidence has been obtained to conclude that they have structures of acetylenic aromatic carotenoids, I (mp 205 °C) and II (mp 194 °C), respectively.



I



II

This is the first establishment of the natural occurrence of acetylenic aromatic carotenoids.

Experimental

Isolation of the Pigments. The extraction and isolation of the pigments were carried out according to the method described in the previous paper.[1] The pigment with a mp of 205 °C was adsorbed between renierapurpurin and renieratene in the chromatogram of the crude pigment mixture, on development on neutral alumina [Merck, deactivated by the addition of water (4%)] with a petroleum ether–benzene mixture (the benzene content being gradually increased from 30 to 75%). The pigment with a mp of 194 °C was adsorbed between renieratene and isorenieratene. Repeated chromatographic separations were necessary to obtain homogeneous zones. Several recrystallizations of the residue of each elute from a mixture of dichloromethane and petroleum ether gave a pure pigment.

Purplish red needles (referred to as the "mp 205 °C pigment"); mp 204—205 °C (uncorr.). UV max. 512, 480, 450 (benzene); 496, 465, 437 nm (*n*-hexane). IR max. (KBr disk); 3024, 2940, 2915, 2850, 1783, 1592, 1560, 1473, 1459, 1440, 1392, 1375, 1318, 1250, 1160, 1005, 960, 883, 830, 803, 776, 728 cm^{-1}.

Red needles (referred to as the "mp 194 °C pigment"); mp 194—194.5 °C (uncorr.). UV max. 500, 470, 442 (benzene); 485, 456, 431 nm (*n*-hexane). IR max. (KBr disk); 3020, 2940, 2910, 2845, 1782, 1620, 1560, 1455, 1436, 1392 1375, 1359, 1158, 997, 960, 878, 830, 805, 723 cm^{-1}.

Instruments. UV Spectra: Hitachi, Model EPS-3T. IR Spectra: Hitachi, Model 215. NMR Spectra: Hitachi, Model R-20B (60 Mc). Mass spectra: Hitachi, Model RMS-4.

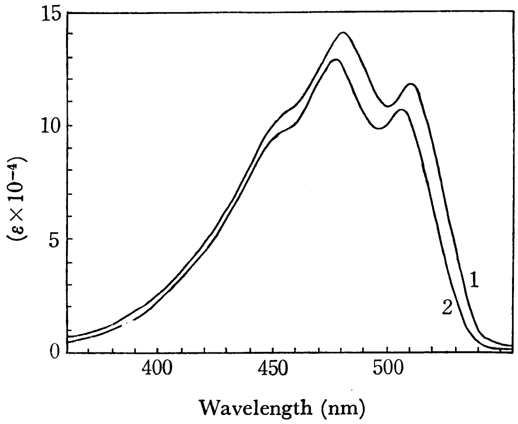


Fig. 1. Absorption spectra of the pigment, mp 205° (1) and renieratene (2) (benzene).

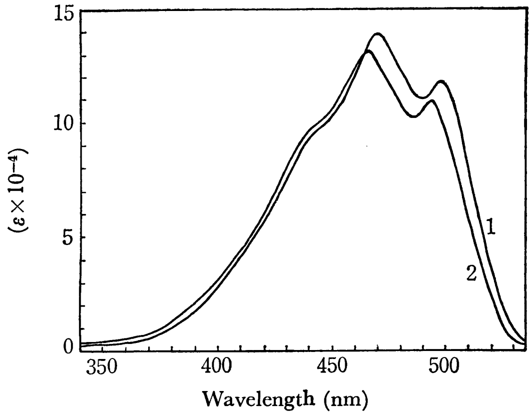


Fig. 2. Absorption spectra of the pigment, mp 194° (1) and isorenieratene (2) (benzene).

Results and Discussion

The Mp 205 °C Pigment. A brief examination of the UV, IR, NMR, and mass spectra of the pigment indicated a structurally very close relationship between the pigment and renieratene [1-(2,3,6-trimethylphenyl)-18-(2,3,4-trimethylphenyl)-3,7,12,16-tetramethyloctadecanonaene].

The mass spectrum of the pigment shows the ions [526(M), 511(M−15), 447(M−79), 434(M−92), 420 (M−106), 405(M−106−15), 393(M−133), 368(M−

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[1] T. Tsumaki, M. Yamaguchi, and T. Tsumaki, *Nippon Kagaku Zasshi*, **75**, 297 (1954); M. Yamaguchi, This Bulletin, **30**, 111 (1957).

[2] M. Yamaguchi, *ibid.*, **30**, 979 (1957); **31**, 739 (1958).

[3] M. Yamaguchi, *ibid.*, **31**, 51 (1958).

[4] M. Yamaguchi, *ibid.*, **33**, 1560 (1960).

158), 328(M−106−92), 301(M−133−92), 287(M−106−133), and 133(base peak)] characteristic of aromatic carotenoids.[5] The ions associated with *m/e* 133 give strong support to the presence of the trimethylphenyl group.[6] Most of the fragments are smaller by two mass units than the corresponding fragments of renieratene [528(M), 449(M−79), 436(M−92), 422 (M−106), 395(M−133), 370(M−158), 330(M−106−92), 303(M−133−92), 289(M−106−133), and 133 (base peak)]. This suggests, besides other less likely structures, a possible formula where one of the double bonds of renieratene is replaced by a triple bond.

The NMR spectrum of the pigment [in $CDCl_3$, an average of 223 times: δ 2.02 (s, 6H) and 2.11 (s, 6H) ("in chain" methyl groups); 2.25 (s, 3H), 2.27 (s, 3H), and 2.34 (s, 6H) (four aromatic methyl groups); 2.45 (s, 6H) (two aromatic methyl groups); 6.10—6.90 (m, 12H) (polyene protons); 6.97 (s, 2H) (ring protons on the 2,3,6-trimethylphenyl group); double doublet centered at 6.99 (H) and 7.30 (H) (J=7.2 Hz, ring protons on the 2,3,4-trimethylphenyl group)] is quite similar to that of renieratene [in $CDCl_3$, an average of 214 times: δ 2.02 (s, 6H); 2.10 (s, 6H); 2.27—2.33 (m, 18H); 6.04—6.84 (m, 14H); 6.97 (s, 2H); 6.99 (H), and 7.29 (H) (dd, J=7.2 Hz)], indicating the presence of 2,3,6- and 2,3,4-trimethylphenyl groups.[7] It is noteworthy, however, that two (δ 2.45) out of six aromatic methyl groups are significantly deshielded when compared with those of renieratene. If the pigment is actually an acetylenic analogue of renieratene, this shift can be reasonably explained by assuming that the location of the triple bond in the polyene chain is in the moiety including the 2,3,6-trimethylphenyl group, probably neighbouring it, as is depicted in I.

The two *ortho*-standing methyl groups are considered to become more deshielded when a double bond attached to the benzene ring is replaced by a triple bond. Similar trends have been observed in alicyclic acetylenic carotenoids.[8,9] The relative abundance of the M−106 or M−92 ion (which stems from the central part of the polyene chain) in the mass spectrum also supports the conclusion.[10] This is also confirmed by the UV spectrum (Fig. 1). The small red shift of $\lambda_{\max}$ (3 nm in benzene) observed in going from renieratene to the pigment can be explained only by assuming that the pigment contains the triple bond in the terminal position of the central conjugated double bond system, as is observed in didehydroastaxanthin relative to astaxanthin[11] or in diatoxanthin[12] and alloxanthin[9,13] relative to zeaxanthin,[14] for example. A triple bond in other positions should give rise to a considerable hypsochromic shift.[15]

The IR spectrum also supports the (I) structure. The absence of $\nu_{C\equiv C}$ can be ascribed to the absence of polar functionality in this disubstituted acetylene. The possibility of the allenic structure, which is often encountered in natural carotenoids,[16] can be completely eliminated by a study of the IR and UV spestra.

The Mp 194 °C Pigment. The same arguments can apply to the pigment with a mp of 194 °C. The mass spectrum [526(M), 511(M−15), 447(M−79), 434(M−92), 420(M−106), 393(M−133), 301(M−133−92), 287(M−133−106), and 133(base peak)] clearly indicates that the compound can be interpreted as a dehydro derivative of isorenieratene [1,18-bis-(2,3,6-trimethylphenyl)-3,7,12,16-tetramethyloctadecanonaene; characteristic ions in the mass spectrum, 528(M, base peak), 513(M−15), 449(M−79), 436(M−92), 422(M−106), 395(M−133), 370(M−158), 330 (M−106−92), 303(M−133−92), 289(M−106−133), and 133]. The NMR spectrum [in $CDCl_3$, an average of 597 times: δ 2.01 (s, 6H), 2.10 (s, 6H), 2.27—2.30 (12H), 2.44 (s, 6H), 6.05—6.90 (m, 12H), and 6.97 (s, 4H)] coincides well with that expected for the proposed formula, II, which has two 2,3,6-trimethylphenyl groups on both ends of the molecule, when compared with the spectrum of isorenieratene [in $CDCl_3$, an average of 223 times: δ 2.02 (s, 6H), 2.10 (6H), 2.31 (18H), 5.95—6.95 (m, 14H), and 6.97 (s, 4H)]. In this case again, a low-field shift by *ca.* 0.16 ppm of the signal of the *ortho*-standing methyl protons can be observed. The UV (Fig. 2) and IR spectra also prove the correctness of the (II) structure. The highest UV max. of the acetylenic analogue is again at a 3—4 nm-longer wavelength location in a benzene solution than that of isorenieratene in the same solvent.

The authors wish to thank Professor Otohiko Tsuge, Research Institute of Industrial Science, of this University, for the help he gave them in the measurements of the mass spectra.

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