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Synthesis of Bis(2,4,5-trimethylphenyl)-, Bis(2,4,6-trimethylphenyl)-, and Bis(3,4,5-trimethylphenyl)tetramethyloctadecanonaene

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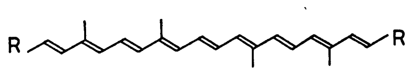
Three isomeric aromatic carotenoid hydrocarbons (I, II, and III) were synthesized, in order to compare them with unidentified minor carotenoid hydrocarbons present in a sea sponge "*Reniera japonica*", known to produce three aromatic carotenoids (IV, V, and VI) as the major constituents of its coloring matter.[1] None of these synthetic products have so far been proved to be identical with those from a natural source.



I R=R′=2,4,5-$(CH_3)_3C_6H_2$-
II R=R′=2,4,6-$(CH_3)_3C_6H_2$-
III R=R′=3,4,5-$(CH_3)_3C_6H_2$-
IV (isorenieratene) R=R′=2,3,6-$(CH_3)_3C_6H_2$-
V (renieratene) R=2,3,6-$(CH_3)_3C_6H_2$-
R′=2,3,4-$(CH_3)_3C_6H_2$-
VI (renierapurpurin) R=R′=2,3,4-$(CH_3)_3C_6H_2$-

Synthesis was carried out according to the conventional $C_{10}+C_{20}+C_{10}$ route,[2] where crocetin dialdehyde was condensed with an appropriate trimethylbenzilidenetriphenylphosphorane.

The highest $\lambda_{\max}$ of the synthetic and natural aromatic pigments are listed in Table 1 in the order of decreasing wavelength. Variations of $\lambda_{\max}$ can be satisfactorily explained in terms of non-planarity between benzene ring and polyene chain, caused by 2- and 6-standing methyl groups and the buttressing effect of 3-standing methyl groups on benzene rings.

Table 1. The highest $\lambda_{\max}$ of aromatic carotenoids

Compound	III	I	VI	V	II	IV
$\lambda_{\max}$ (benzene, mμ)	491	490	486	477	471	466

The pigments were adsorbed on alumina (Merck, neutral; Grade II: from benzene solution) in the following sequence of decreasing adsorbability: III, VI, I, V, II, IV.

Experimental

Materials. 2,4,5-, 2,4,6-, and 3,4,5-Trimethylbenzyl alcohol were prepared by lithium aluminium hydride reduction of the corresponding methyl trimethylbenzoates. The recrystallized alcohols melted at 83—83.5°C (lit, 83—83.5°C[3]), 86.5—87°C (lit, 87—88°C[4]) and 74—75°C (lit, 78°C[5]), respectively.

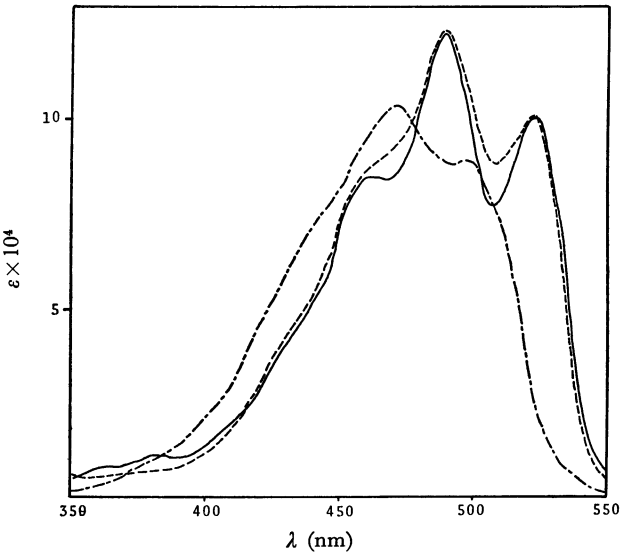


Fig. 1. Absorption curves of I (----), II (—·—·), and III (——) (benzene).

(Trimethylbenzyl)triphenylphosphonium Bromides. These were prepared from the corresponding alcohols in a similar way to that described by Cooper *et al.* on analogous phosphonium bromides.[6] (2,4,5-Trimethylbenzyl)triphenylphosphonium bromide: colorless prisms, mp 204—205°C (Found: C, 70.79; H, 6.32. Calcd for $C_{28}H_{28}BrP$: C, 70.74; H, 5.94%). 2,4,6-Trimethylbenzyl analogue: colorless needles, mp 243—245 °C (Found: C, 69.70; H, 6.15%). 3,4,5-Trimethylbenzyl analogue: colorless plates, mp 250—252 °C (Found: C, 70.20; H, 6.29%).

1,18-Bis(2,4,5-trimethylphenyl)-3,7,12,16-tetramethyloctadecanonaene (I). An ethereal solution of phenyllithium (0.8 M, 0.4 ml) was added to a stirred suspension of (2,4,5-trimethylbenzyl)triphenylphosphonium bromide (121 mg) in ether (4 ml). After stirring for one hour, two drops of methylene chloride were added to destroy excess base. A solution of crocetindial[7] (25 mg) in methylene chloride (1 ml) was then added, and the mixture was stirred under reflux for four hours. The mixture was diluted with methanol (50 ml), and kept at 0 °C overnight. The precipitate was washed with boiling methanol several times and recrystal-

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lized from a mixture of chloroform and ethanol giving I as purple plates, 18.6 mg, m. p. 208—210°C (evacuated capillary). $\nu_{\max}$ (KBr disk); 3020, 2990, 2930, 2875, 1565, 1502, 1460, 1446, 1398, 1368, 1320, 1267, 1196, 1180, 1025, 1003, 964, 875, 845, 825, and 690 cm^{-1}. UV spectrum; Fig. 1.

1,18-Bis(2,4,6-trimethylphenyl)-3,7,12,16-tetramethyloctadecanonaene (II). This was prepared in a similar way to that for (I). Purple red plates, 10 mg, mp 199—200°C. $\nu_{\max}$ 3020, 2990, 2910, 2860, 1608, 1560, 1475, 1443, 1395, 1376, 1365, 1030, 1006, 967, 854, 825, 805 and 726 cm^{-1}. UV spectrum; Fig. 1.

1,18-Bis(3,4,5-trimethylphenyl)-3,7,12,16-tetramethyloctadecanonaene (III). This was prepared in a similar way to that for (I). Purple plates, 10 mg, mp 215—216°C. $\nu_{\max}$; 3020, 2920, 2860, 1600, 1555, 1480, 1440, 1390, 1365, 1295, 1155, 1030, 1006, 960, 873, 838, 828, 765, and 705 cm^{-1}. UV spectrum; Fig. 1.