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PARTIAL SYNTHESIS OF AROMATIC CAROTENOIDS, TEDANIN, AGELAXANTHIN A, TETHYATENE, AND RENIERATENE

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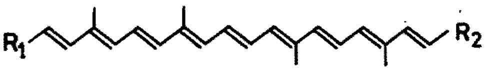
Sammary: Aromatic carotenoids, tedanin, agelaxanthin A, and tethyatene were synthesized from O-acetyl-β-citraurin derived from natural zeaxanthin, and tethyatene was further transformed into renieratene as the first example of aromatization of an alicyclic ring in carotenoids.

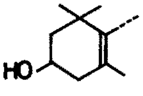
Zeaxanthin (2) extracted from the seeds of *Euonymus japonica*¹⁾ was acetylated and oxidized to O-acetyl-β-citraurin (1; mp 145°C) by known method.$^{2)}$ 1 reacted with 2,3,4-trimethylbenzyltriphenylphosphonium bromide$^{3)}$ in 1,2-epoxybutane in a sealed tube for 20 h at 80°C to give 3 (60%; mp 165°C) which was saponified$^{4)}$ to the alcohol [4; 98%; mp 176-177°C; $\lambda_{max}{}^{4)}$ 488, 459, 437 nm; NMR(δ)$^{4)}$ 0.96(s, 6H), 1.66(s, 3H), 1.90(s, 9H), 1.99(s, 3H), 2.14(s, 3H), 2.24(s, 6H)]. Oxidation of 4 with DMSO, TFA, pyridine, and dicyclohexylcarbodiimide in benzene for 5 h led to 5 [70%; mp 186°C; λ_{max} 488, 458, 436 nm; NMR 1.11(s, 6H), 1.82(s, 3H), 2.00(s, 9H), 2.08(s, 3H), 2.23(s, 3H), 2.31(s, 6H)]. Stirring a mixture of 5, acetic anhydride, and 4-dimethylaminopyridine in dichloromethane for 20 h gave 6 [72%; mp 175°C; λ_{max} 466 nm; NMR 1.10(s, 6H), 1.89(s, 3H), 1.98(s, 9H), 2.05(s, 3H), 2.10(s, 3H), 2.20(s, 3H), 2.28(s, 6H)]. Epoxidation of 6 at the 3,4-double bond was unsuccessful. 6 was then oxidized with t-butyl hydroperoxide in benzene for 2 h under the presence of methanolic benzyltrimethylammonium hydroxide to 7 (5%; mp 189-190°C) which was identical with tedanin$^{5)}$ in every respect examined (UV, NMR, MS, and mixed mp). Tedanin has been isolated from japanese sea sponges, *Tedania digitata*$^{6)}$ and *Clathria frondifera*.$^{7)}$

Reaction of 1 with 2,3,6-trimethylbenzyltriphenylphosphonium bromide$^{3)}$ in 1,2-epoxybutane for 8 days at 100-105°C led to 8 (17%; λ_{max} 474, 448, 425 nm), which on saponification gave 9

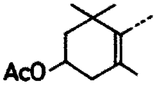
1 R_1= *B*



2 R_1= R_2= *A*
3 R_1= *B*, R_2= *C*
4 R_1= *A*, R_2= *C*
5 R_1= *D*, R_2= *C*
6 R_1= *E*, R_2= *C*
7 R_1= *F*, R_2= *C*
8 R_1= *B*, R_2= *G*
9 R_1= *A*, R_2= *G*
10 R_1= *H*, R_2= *C*
11 R_1= *G*, R_2= *C*



A



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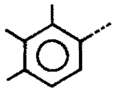

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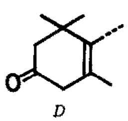

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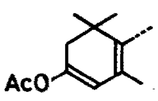

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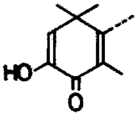

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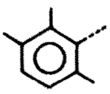
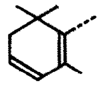


G



H

(95%; mp 182°C). 9 showed good agreement with the reported data (UV, NMR, MS) of agelaxanthin A which has been isolated from a sea sponge of West Indies, *Agelas schmidtii*.[8]

When 4 was stirred with methyl ester of carboxysulfamoyltriethylammonium hydroxide inner salt[9] in benzene for 3 h, the corresponding N-(methoxycarbonyl)sulfamate was formed as amorphous powder which was then refluxed with sodium t-butoxide in benzene for 40 min. The product [10; 27% from 4; mp 165°C; NMR 1.04(s, 6H), 1.88(s, 3H), 1.99(s, 9H), 2.06(s, 3H), 2.21(s, 3H), 2.30(s, 6H)] showed good agreement with the reported data (UV, IR, and MS) of tethyatene isolated from a japanese sea sponge, *Tethya amamensis*.[10]

Treatment of 10 with excess γ-manganese dioxide[11,12] in a mixture of dichloromethane and acetone for 50 min gave renieratene (11, 10%; mp 187-188°C) as a sole isolable product. It was identical with the natural specimen isolated from a sea sponge, *Reniera japonica*,[13] in every detail (UV, IR, NMR, MS, and mixed mp). Further studies on aromatization of other substrates are in progress.

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References and Notes

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