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REVISION OF THE STRUCTURES OF THE BACTERIAL C_{50}-CAROTENOIDS C.p. 450 AND C.p. 473*

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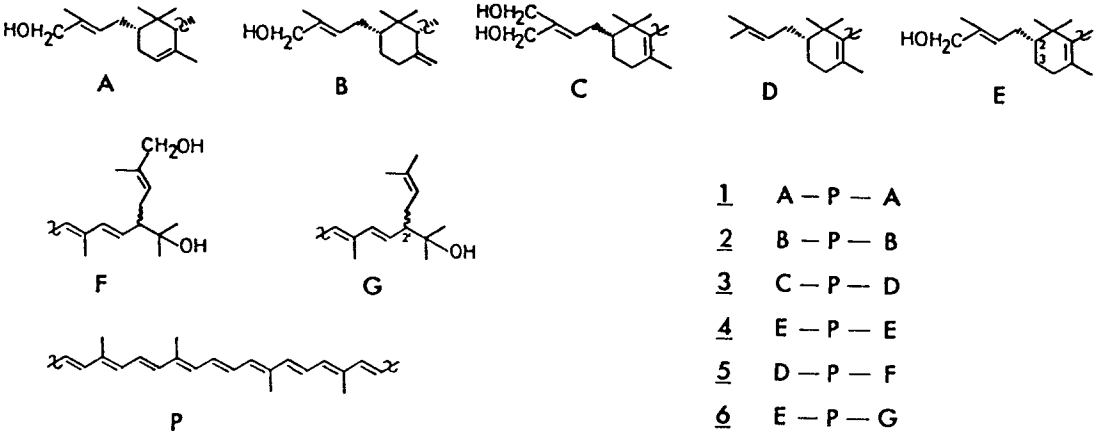
Key words: C_{50}-carotenoids; revision; (2R,2'R)-2,2'-bis(4-hydroxy-3-methyl-2-butenyl)-β,β-carotene; 2-(4-hydroxy-3-methyl-2-butenyl)-2'-(3-methyl-2-butenyl)-1',2'-dihydro-β,ψ-caroten-1'-ol; LIS ^{1}H NMR.

The bacterial C_{50}-carotenoid diols decaprenoxanthin from Flavobacterium dehydrogenans, **1**[1-3], with substituted ε-end groups A and sarcinaxanthin from Sarcina lutea, **2**[4], with substituted ψ-end groups B have been assigned centro-



1 A — P — A
2 B — P — B
3 C — P — D
4 E — P — E
5 D — P — F
6 E — P — G

Scheme 1.

*Part 21 in the series C_{50}-carotenoids. For Part 20 see Acta Chem.Scand. B33 (1979) 551.

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symmetrical structures, Scheme 1. In contrast, the C_{50}-carotenoid C.p. 450 from Corynebacterium poinsettiae has been formulated as the unsymmetrical 3[5,6] with the differently substituted β-end group C containing both prim. allylic hydroxy groups and a hydrocarbon end group D.

The unsymmetrical assignment of C.p.450 (3) was based on the ^{1}H NMR spectrum with signals at δ 1.69 and 1.61 in ratio 3:1 and M-128 ($C_{39}H_{54}$) and M-212 ions in the mass spectra of the parent diol and the diacetate respectively, rationalized as RDA cleavage of end group C[4].

Recently, Milborrow[7] has claimed in a review the isomerization of sarcinaxanthin (2) to decaprenoxanthin (1) and a "symmetrical C.p. 450" in 0.06 M potassium hydroxide. Supporting experimental details were not given.

C.p. 450 has now been reisolated from C.poinsettiae and crystallized. Its ^{1}H NMR spectrum, lacking the signal at δ 1.61 clearly reveals a centrosymmetrical structure 4 (E-P-E) both in the absence and presence of Eu(fod)$_3$. The chemical shifts for the gem. - dimethyl groups of the β-rings clearly favour 2,2'-substitution rather than 3,3'-substitution in comparison with relevant models[1,8,9]. CD evidence[6] requires 2-or 3-substituted β-rings. The configurational assignment of C.p. 450[6] still remains valid since the positions of the hydroxy groups on the isopentenyl substituents do not affect the CD spectrum. C.p. 450 thus is (2R,2'R)-2,2'-bis(4-hydroxy-3-methyl-2-butenyl)-β,β-carotene (4).

The monocyclic C_{50}-diol C.p. 473 from C.poinsettiae was previously assigned structure 5[5] with the tert.hydroxy group and the prim. allylic hydroxy group on the same aliphatic end group F and a hydrocarbon substituted β-end group. ^{1}H NMR analysis could not distinguish between 5 (D-P-F) and 6 (E-P-G). The preference for assignment 5 versus 6 was based on the fragmentation pattern upon electron impact; in particular a $C_{39}H_{54}$ fragment ion for 5, compatible with cleavage of the 4',5' single bond accompanied by hydrogen transfer.

Reisolation of C.p.473 from the same source for ^{1}H NMR LIS experiments has been carried out. The results clearly favour structure 6 (E-P-G) for C.p. 473 with the two hydroxy groups at opposite ends of the molecule. Thus, the protons in both end groups were strongly influenced by the shift reagent. Again chemical shift considerations are consistent with 2-substitution of the β-ring (E), and 2'-substitution in the aliphatic end group G is compatible with the MS fragmentation and the H-3' signal at 100 MHz (δ5.50 dd, $J_{2',3'}$= 7 Hz, $J_{3',4'}$= 14 Hz; cfr. Ref.10 for tetradesoxybacterioruberin), in the present case somewhat obscured by the olefinic proton of the hydroxylated isopentenyl end group

(δ 5.44 broad t, J=ca.7 Hz; cfr. C.p. 450 (4), but unequivocal with 400 MHz. The revised structure 2-(4-hydroxy-3-methyl-2-butenyl)-2'-(3-methyl-2-butenyl)-1', 2'-dihydro-β,ψ-caroten-1'-ol (6) is consequently assigned to C.p. 473.

The chirality of C.p. 473 (6) as well as of the aliphatic C_{45}-carotenoid 2-isopentenyl-3,4-dehydrorhodopin (C.p. 482)[5,8] with the same chiral end-group G is currently being studied.

C.p. 450 (4).

Vis: λ_{max} (acetone) nm; (437), 450, 478; % III/II[11] = 38.

R_F: TLC (SiO_2) 0.17 (acetone-hexane 30+70), 0.52 (EtOAc-benzene 25+75).

^1H NMR ($CDCl_3$, 100 MHz) δ :1.98 (four in-chain methyl); 1.70 (two end-of-chain methyl and two isopropylidene); 1.07, 0.92 (two pairs of non-equivalent gem.-methyl groups); 4.03s (two prim. allylic methylene); 5.44t broad (J=ca.7 Hz) (two isopropylidene olefinic protons). End group resonances were consistent with reported values.[8]

with $Eu(fod)_3$: molar conc. Eu(fod)/carotenoid ranging from 0.5-2.0 all end-group signals shift symmetrically downfield. In-chain methyls unaffected.

MS: m/z = 704 (M-100%), M-18 (6%), M-92 (26%), M-106 (8%).

C.p.473 (6).

Vis: λ_{max} (acetone) nm; (449), 473, 504; % III/II = 38.

R_F: TLC (SiO_2) 0.53 (acetone-hexane 35+65).

^1H NMR ($CDCl_3$, 100 MHz) δ :1.98 (four in-chain methyl); 1.93 (one in-chain/end-of-chain methyl); 1.19, 1.23 (two methyls attached to tert. hydroxyl); 1.70 (three methyls; one end-of-chain in β-ring and two isopropylidene methyls); 1.61 (isopropylidene methyl at acylic end); 1.07, 0.92 (non-equivalent gem.-methyls on β-end); 4.04 (two prim. allylic methylene groups); 5.05m (olefinic isopropylidene proton at aliphatic end); 5.45 broad t (J= ca. 7 Hz, olefinic isopropylidene proton at β-end). 5.50dd (J_1=7 Hz, J_2=14 Hz, terminal olefinic proton aliphatic end).

with $Eu(fod)_3$: molar conc. ranging from Eu(fod)/carotenoid 0.5-2.0 effects downfield shift of hydroxymethyl groups as well as gem.-methyls on β-end while in-chain methyls unaffected.

MS: m/z = 704 (M, 100%), M-18 (13%), M-58 (13%), M-92 (13%), M-108 (73%), M-108 (13%), M-128 (5%).

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