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Bacterial Carotenoids LI*

C_{50}-Carotenoids 17**

TOTAL SYNTHESIS OF TWO BACTERIORUBERIN DERIVATIVES

ABSOLUTE CONFIGURATION OF BACTERIORUBERIN

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No C_{50}-carotenoids of the 2,2'-isopentenyl substituted carbon skeleton encountered in naturally occurring carotenoids have hitherto been synthesized

Absolute configurations have recently been assigned to bicyclic C_{50}-carotenoids with β,ε or γ-end groups,[1-3] but the chirality of aliphatic end groups in C_{50}-carotenoids has remained unsolved.[4]

In this priority note we report the synthesis of optically inactive tetraanhydrobacterioruberin (1) from racemic lavandulol (2) via the intermediates 3,5-7, using crocetindial (8) as the central component, Scheme 1 Tetraanhydrobacterioruberin (1) thus prepared had electronic and mass spectra and chromatographic properties identical with those of 1 prepared from naturally occurring bisanhydrobacterioruberin (9) or bacterioruberin (10) on a micro scale by known methods,[5] thereby confirming the constitutions of 1, 9 and 10.

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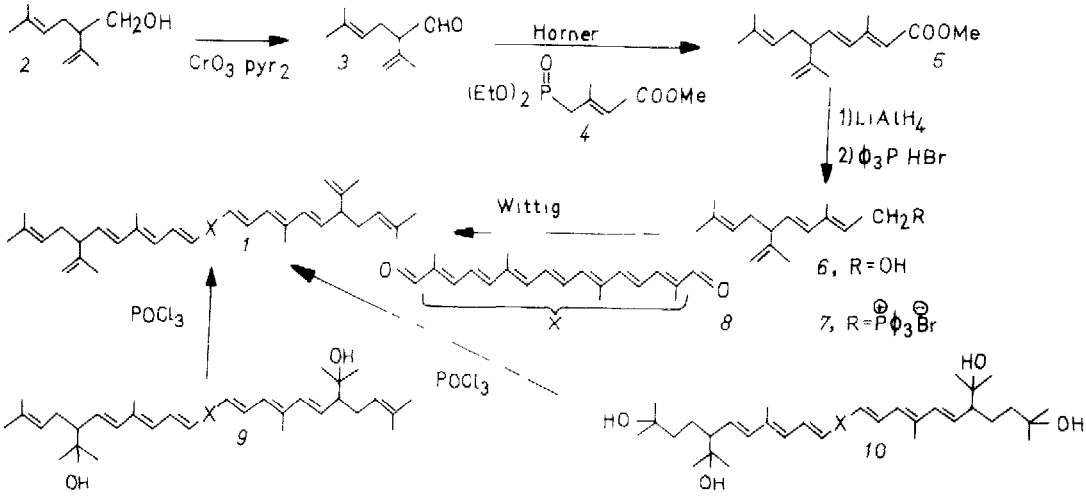
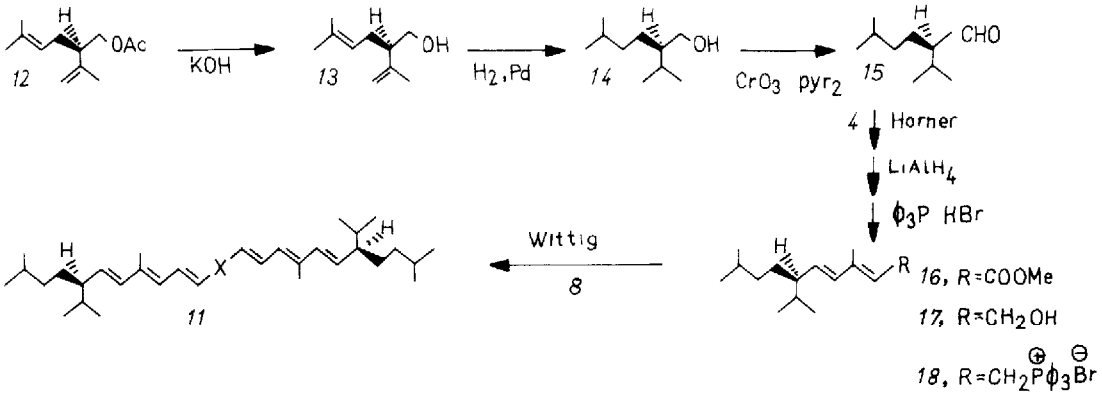
* Part L. Arch. Mikrobiol. In press.

** Part 16. Acta Chem. Scand. In press.



Scheme 1

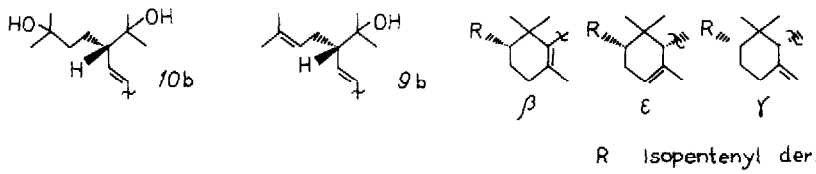
We further report the synthesis of (2R,2'R)-octahydro-tetraanhydrobacterioruberin ≡ tetradesoxybacterioruberin (11) from (-)-(R)-lavandulyl acetate (12) via the intermediates 13-18 as depicted in Scheme 2 The synthetic model 11 had electronic, IR, ^{1}H NMR and mass spectral properties consistent with structure 11 The CD spectrum of the synthetic C_{50}-model 11 exhibited a Cotton effect opposite to that of natural bacterioruberin (10) or bisanhydrobacterioruberin (9) Provided octahydro-tetraanhydrobacterioruberin (11) is a valid model for CD comparison with bacterioruberin (10) and bisanhydrobacterioruberin (9), opposite configuration at C-2,2' of (-)-(R)-lavandulol (13)[6] and naturally occurring 9 and 10 could be concluded



Scheme 2.

However, for confirmation of the above conclusion total synthesis of optically active tetraanhydrobacterioruberin from (-)-(R)-lavandulol (13) was subsequently effected by the same route as outlined in Scheme 1 The resulting (2S,2'S)-tetraanhydrobacterioruberin (1b) unexpectedly showed the same CD as tetraanhydrobacterioruberin ex natural bacterioruberin, demonstrating that a direct comparison of CD properties of bacterioruberin (10) and bisanhydrobacterioruberin (9) with the synthetic octahydro model (11) was not valid, contrary to previous assumptions.[7]

Since tetraanhydrobacterioruberin prepared by total synthesis from (-)-(R)-lavandulol (13)[6] and by partial synthesis from natural bacterioruberin (10) and bisanhydrobacterioruberin (9) have the same CD properties bacterioruberin has (2S,2'S)-chirality (10b) and natural bisanhydrobacterioruberin the same (2S,2'S)-configuration (9b), that is the same configuration as cyclic C_{50}-carotenoids with β,ε and γ-rings, Scheme 3



Scheme 3

Biogenetically the results could indicate that isopentenylation of C_{40}-carotenoids to C_{45}- and C_{50}-carotenoids was a common step for aliphatic and cyclic C_{50}-carotenoids, preceding cyclization or hydroxylation. However, more plausible concerted mechanisms for isopentenylation/cyclization and isopentenylation/hydroxylation are also consistent with the present findings.

Synthesis of optically inactive bacterioruberin is in progress. Experimental details will be published

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1. Andrewes, A.G , Liaaen-Jensen, S and Borch, G. , Acta Chem. Scand B 28, 737 (1974)
2. Andrewes A.G Liaaen-Jensen, S. and Weeks, O.B , Acta Chem. Scand. B 29, 884 (1975).
3. Hertzberg, S. and Liaaen-Jensen, S., Abstr 4th Int. IUPAC Symp. Carot. 1975, p 18.
4. Borch, G , Norgård, S. and Liaaen-Jensen, S., Acta Chem Scand. 25, 402 (1971).
5. Kelly, M., Norgård, S. and Liaaen-Jensen, S Acta Chem Scand. 24, 2169 (1970).
6. Souček, M. and Dolejš, L., Collect. Czech. Chem. Commun 24, 3802 (1959).
7. Liaaen-Jensen, S. Pure and Applied Chem. In press.