Tetrahedron Letters No. 43, pp 3743 - 3744, 1975. Pergamon Press. Printed in Great Britain.

ACID CATALYZED DEHYDROGENATION AND RETRO REARRANGEMENT OF 2-HYDROXYLATED ß,ß-CAROTENES.

Hartmut Kayser
Department of Biology I, University of Ulm,
D-7900 Ulm/Do., P.O.Box 4066, Germany

(Received in UK 7 August 1975; accepted for publication 15 September 1975)

Recently, for the first time the natural occurence of bicyclic carotenoids hydroxylated at the 2-position was demonstrated in a green alga containing ß,ß-caroten-2-ol (1a), ß,ε-caroten-2-ol, and ß,ß-carotene-2,2'-diol (2a) [1], and in crustacea containing only 1a [2].

During own work 1a and 2a were isolated in large amounts from several insect species [3,4], the report on 2a being the first one for an animal [4]. The structure of 1a was based on its electronic spectrum (λ_{max} 450,475 nm; acetone), IR-spectrum (ν_{max} 3450,1020,963 cm^{-1}; KBr), mass spectrum (m/e 552; M^+; $C_{40}H_{56}O$), and basically on its ^1H-NMR spectrum (τ 6,43; $CDCl_3$) [3].

1a undergoes a very specific reaction under acidic conditions. Treatment with 0,1 m BF_3-etherate in chloroform yielded a less polar product to which structure 1b was attributed on the following basis:

Electronic spectrum: λ_{max} 432,456,485 nm (acetone), indicating eleven conjugated double bonds and retro structure.

IR-spectrum: ν_{max} 1735 cm^{-1} (isolated carbonyl), doublet at 953,976 cm^{-1} (retro structure)

Mass spectrum: m/e 550 (M^+); $C_{40}H_{54}O$. The endocyclic double bond was located in the non-oxygenated ring on the basis of fragment ions.

Chemistry: yielded no acetate in contrast to 1a.

Conclusively, treatment with BF_3 results in the dehydrogenation of the secondary alcohol group combined with a retro rearrangement of the polyene system. This reaction is quite different from the wellknown dehydrogenating action of BF_3 and other Lewis acids in an inert medium [5]: the BF_3 concentration is much lower in the reaction, reported here, and allows only to a very low exten~~d~~t the formation of blue complexes; furthermore, the reaction is restricted not to an inert solvent or to BF_3, but proceeds also with HCl and in ethanol.

The diol 2a (λ_{max} 450,475 nm, acetone; m/e 568, M^+; $C_{40}H_{56}O_2$) showed an analogous reaction on treatment with BF_3-chloroform. The less polar product

2b had properties as follows:

Electronic spectrum: λ_{max} 418,442,471 nm (acetone), demonstrating a retro structure with ten conjugated double bonds.

Mass spectrum: m/e 566 (M^+), $C_{40}H_{54}O_2$.

Chemistry: yielded no acetate.

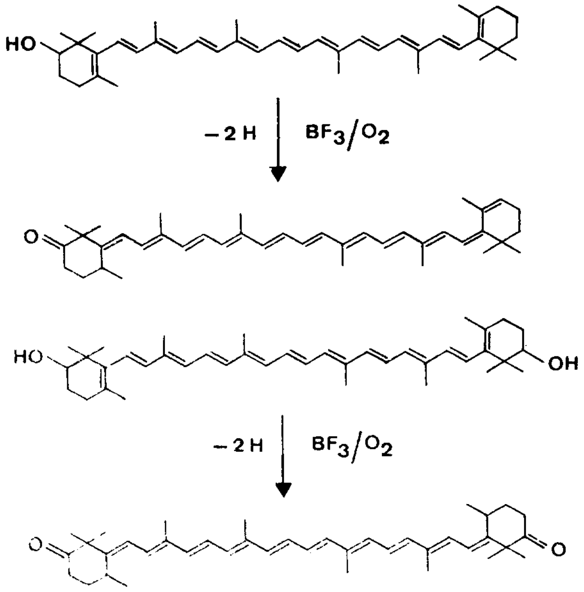
For the latter reason it was proposed that the second hydroxyl group was converted to a carbonyl function by migration of one double bond of the polyene chain. This is in agreement with its electronic spectrum showing the shortening of the chromophore by one double bond.

Comparison between the dehydrogenations performed in pure oxygen and under nitrogen revealed that O_2 may be the acceptor for the eliminated hydrogen.

The reaction described here is new in carotenoid chemistry, and seems to be specific for 2-hydroxylated compounds. It is up to now the first one for the 2-ol structure besides acetylation. Therefore, it is of diagnostic value for the identification of 2-hydroxylated carotenoids.
The results will be presented in detail in the full papers [3,4].

References

1. Kjøsen,H., Arpin,N. and Liaaen-Jensen,S., Acta Chem.Scand.26,3053(1972)
2. Lee,W.L. and Gilchrist,B.M., Comp.Biochem.Physiol.51B,247(1975)
3. Kayser,H., Z.Naturforsch., in preparation.
4. Kayser,H., Z.Naturforsch., in preparation.
5. Petracek,F.J. and Zechmeister,L., J.Amer.Chem.Soc.78,3188(1956)



1a

1b

2a

2b