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NOVEL CAROTENOID 3,6-EPOXIDES FROM RED PAPRIKA, CAPSICUM ANNUUM

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Summary: The new carotenoid pigments (2),(3),(7),(9) and (10) have been isolated from red paprika; the 3,6-epoxy-5-hydroxy end group present in the pigments (2) and (9), hitherto has not been reported amongst natural carotenoids.

Paprika, Capsicum annuum is one of the oldest and most important carotenoid food colours, and it is widely used as a condiment in chili products.[1] The constitutions of the carotenoid pigments produced by paprika have been investigated in detail. Some twenty carotenoids hitherto have been isolated with capsanthin(5) and capsorubin(8) representing the most abundant.[2] In connection with investigations of the biosynthetic inter- relationships amongst paprika pigments, we have examined the carotenoid contents of C.annuum in further detail. In this Letter we describe the structures of a number of new oxygenated carotenoid pigments, including the novel and unusual carotenoid 3,6-epoxides(2) and (9).

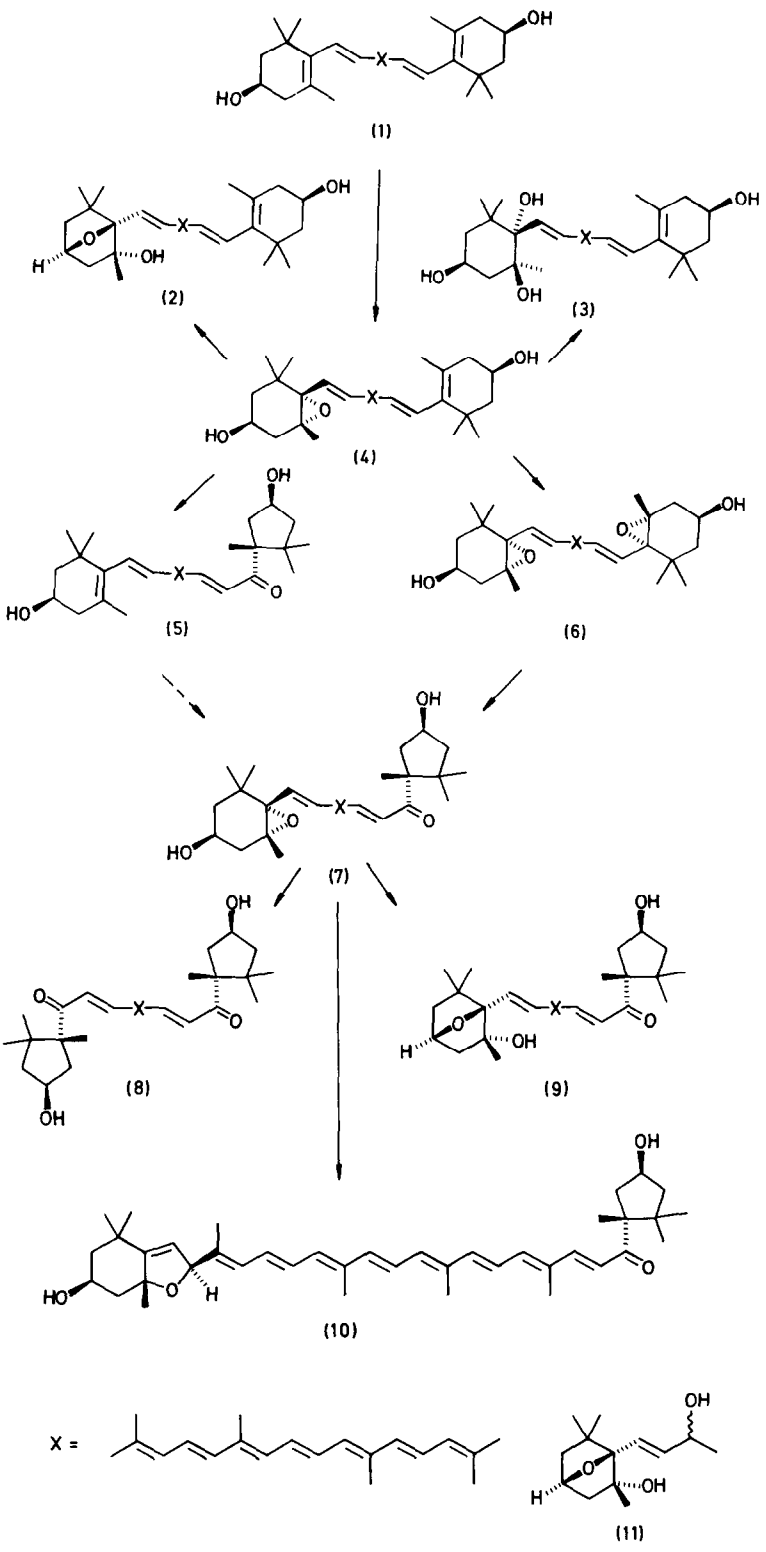
Chromatography of extracts from pods of red paprika (deactivated $CaCO_3$ using C_6H_6-Me_2CO mixtures), followed by re-chromatography of the separated fractions, gave in addition to known carotenoids[3], five new pigments each of which was obtained as a highly crystalline solid. The structures of these compounds were determined by a combination of FAB mass spectrometry, visible absorption, 250MHz p.m.r. and ^{13}C n.m.r. spectroscopy. In addition, iodine-catalysed equilibration studies were carried out to ascertain the geometries about the polyene portions of the structures, and absorption data were routinely investigated in the presence and absence of acid and sodium borohydride.

Two new minor carotenoids isolated were capsanthin 5,6-epoxide(7), red needles, m.p. 177-8°C, $[\alpha]_D$ + 9.4°(C_6H_6) and 'capsochrome'(10), yellow needles, m.p. 180-02°C. This is the first time that capsanthin 5,6-epoxide (7) and capsochrome have been obtained in pure, crystalline form, and their structures have been only tentatively assigned earlier.[4] Capsochrome(10) is isomeric with the epoxide(7), and indeed acid treatment of a benzene

solution of the latter ($_{max}$453, 478, 505nm) produced the same chromophore (λ_{max}440, 460, 485nm) found in capsochrome[4]; this conversion corresponds to the well known 'epoxide-furan oxide' rearrangement.[5] The p.m.r. shift data for the cyclopentane ring hydrogen atoms of capsochrome(10), correlated well with data for capsanthin 5,6-epoxide(7). Furthermore, the two broad singlets at δ5.07 and δ5.31 are diagnostic for the dihydrofuran part structure with the 2,5-substituents cis-to one another.[6]

The major new pigment to be isolated from paprika, red prisms, m.p. 169-170°C, $[\alpha]_D$ + 3.2°(C_6H_6), λ_{max}(C_6H_6) 458(89,400), 479(106,200), 505(81,000) nm., was shown to have the novel capsanthin 3,6-epoxide structure(9). Like capsochrome(10), the new pigment was found to be isomeric with capsanthin 5,6-epoxide(7), and comparative p.m.r. spectral data fully supported the identity of the cyclopentane ring portions of the three molecules. In addition, treatment of (9) with sodium borohydride produces an identical hypsochromic shift in the visible spectrum (i.e. 458, 479, 505 -> 425, 451, 482nm) to that observed with both capsanthin 5,6-epoxide and capsochrome. The p.m.r. spectrum of (9) displays a characteristic signal at δ5.76(d, J15) suggesting a trans(E)-disubstituted double bond at the terminus of the polyene segment of the molecule, and attached to a quaternary sp^3-hybridised carbon centre carrying an oxygen atom.[7] These data, taken together with the apparent triplet at δ4.39 in the p.m.r. spectrum, suggested a carotenoid 3,6-epoxide end grouping in the molecule. This assignment was further supported, when a comparison of p.m.r. data was made with those of the natural product(11) found in tobacco.[5] To our knowledge this is the first time the 7-oxabicyclo[2.2.1]-heptanol (viz 5-hydroxy-5,6-dihydro-3,6-epoxy) end group has been found in a natural carotenoid.[8] It seems probable that both capsochrome(10) and capsanthin 3,6-epoxide(9) are derived in Nature from the epoxide(7). Capsanthin 5,6-epoxide(7) has its biosynthetic origins in zeaxanthin(1) and antheraoxanthin(4) via violaxanthin(6), or alternatively via capsanthin(5).[9]

The remaining two new carotenoids isolated from paprika in this study were found to have the structures (2) and (3) containing identical 3-hydroxycyclohex-5-ene end groups. The structure of the carotenoid 3,6-epoxide(2), yellow plates, m.p. 164-5°C, followed conclusively from comparison of its spectroscopic properties with those of (9) and zeaxanthin(1), whereas the structure of the interesting tetrol(3), yellow crystals, m.p. 174°C rested on comparison of spectroscopic data with those published for similar compounds, e.g. heteroxanthin, karpoxanthin, by Liaaen-Jensen and Eugster and their respective collaborators.[10] These two metabolites no doubt represent a branching point from antheraoxanthin(4) in the biosynthesis of the more common carotenoid pigments produced by


(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
X =
(11)

paprika. These relationships are summarised in the accompanying flow diagrams.

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