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Capsoneoxanthin, a new carotenoid isolated from the fruits of *Asparagus falcatus*

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Abstract

From the ripe fruits of *Asparagus falcatus* capsoneoxanthin, a minor carotenoid was isolated and, based on its spectral data, identified as (all-*E*,3*S*,5*R*,6*R*,3′*S*,5′*R*)-6,7-didehydro-5,6-dihydro-3,5,3′-trihydroxy-β,κ-caroten-6′-one.

Keywords: carotenoids; isolation; structure elucidation; asparagus.

Neoxanthin was first isolated from the green leaves of barley by Strain[1] in 1938, and was subsequently shown to be one of the principal xanthophylls in a wide variety of seed plants and spore-bearing plants. The structural elucidation of the allenic end group of neoxanthin was performed in 1969 by Cholnoky and co-workers.[2] Since that time further carotenoids containing allenic end groups have been isolated. Fucoxanthin and peridinin, the two carotenoids biosynthesised in the largest quantity on our planet, have been isolated from several classes of algae.[3] Neoflor and 6-epineoflor have been isolated from petals of *Trollius europeus*.[4]

In a previous paper we described the isolation and identification of capsanthin, capsorubin, 5,6-diepikarpoxanthin, capsochrome, capsanthin 5,6-epoxide, mutatoxanthin, antheraxanthin and capsanthone from the fruits of *Asparagus falcatus*.[5] During the isolation procedure of these carotenoids, HPLC investigations showed that the most polar fraction contained a significant amount of new carotenoid. In this paper, as a continuation of these studies, the isolation of a hitherto unknown carotenoid and its structure elucidation are reported.

During the isolation of 5,6-diepikarpoxanthin, several polar carotenoids were observed by column chromatography.[5] A compound which was absorbed between the *cis*-isomers of capsanthin and capsorubin on the $CaCO_3$ column (*Biogal*, Hungary) was further investigated. By repeated column chromatography, a new carotenoid, for which the name 'Capsoneoxanthin' is proposed, was isolated and crystallised from benzene/hexane (1.1 mg red crystals; mp

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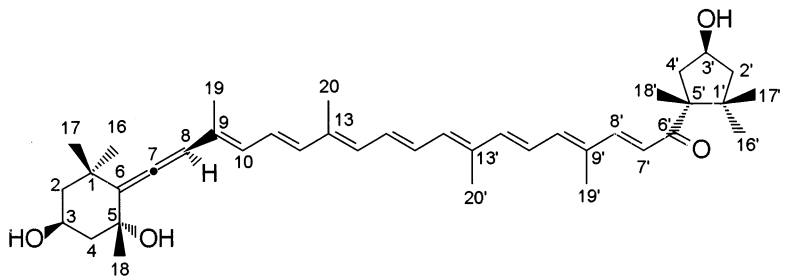
161–163°C). Its UV–Vis spectrum revealed maxima at 508 and 478 nm, (in benzene, no *cis* peak), identical with the spectrum of capsanthin 5,6-epoxide. However, no reaction took place with HCl/AcOH indicating that a 5,6-epoxy group was not present. Reduction of the compound with $NaBH_4$ gave a mixture (ca. 1: 1) of the corresponding stereoisomeric alcohols which was separated by HPLC. The UV–Vis spectrum of this mixture exhibited, as expected, an increased fine structure and a hypsochromic shift (486, 464 nm in benzene). The HPLC-MS analysis showed a signal for a molecular ion at m/z 600 (100, M^+), which corresponded to $C_{40}H_{56}O_4$. Fragmentation peaks could be observed at m/z 582 ($[M-H_2O]^+$), 564 ($[M-2H_2O]^+$), and 494.

Detailed structural information about the constitution and configuration of the new compound was derived from NMR experiments. The ^1H and ^{13}C assignments were based on ^1H, ^1H–^1H COSY and ^{13}C–^1H HSQC measurements. The ^1H and ^{13}C chemical shifts and the $J_{H,H}$ coupling constant values determined from the NMR spectra corresponded with literature values for the chemical shifts of an allenic and a κ end group.[6] The ^1H NMR data of capsoneoxanthin was completely in accordance with its presented constitution and configuration.[7] The chemical shift of the allenic proton was obtained at 6.03 ppm. Based on the diagnostically relevant ^1H NMR data that have been reported by Baumeler and Eugster[8] and on our own NMR results, the configuration of the allenic end group of the capsoneoxanthin was assigned as 3*S*,5*R*,6*R*. All allenic carotenoids that have been isolated from nature have the 3*S*,5*R*,6*R* configuration. The possible natural occurrence of (6*S*)-neoxanthin, fucoxanthin or peridinin has been questioned. The (6*S*)-isomers of these carotenoids have only been prepared by iodine-catalysed stereomutation of (6*R*)-compounds.[9,10]

Because of the small amount of available sample, so ^{13}C and ^{13}C–^1H HMBC experiments could not be performed, thus for the assignment of the protonated carbon resonances a ^{13}C–^1H HSQC experiment was used. The ^{13}C signals of the olefinic range could only be partially assigned.[7]



Capsoneoxanthin
(all-*E*,3*S*,5*R*,6*R*,3'*S*,5'*R*)-6,7-didehydro-5,6-dihydro-3,5,3'-trihydroxy-β,κ-caroten-6'-one

The CD spectra of capsoneoxanthin, which had positive maxima at 242, 308 and 351 nm and negative maxima at 217, 255 and 286 nm, showed a similar curve to those of neoxanthin. However, the location of the main maxima and minima in the CD spectrum of the capsoneoxanthin did not correspond to that reported for neoxanthin.[8] It is known that the CD spectrum of neoxanthin is mainly dictated by the epoxidic end group with little contribution from the allenic end group[11] thus, the CD spectrum did not give any indication as to the chirality of the allenic end group.

It has been assumed that the allenic group originates from proton abstraction from C7 neighbouring the 5,6-epoxy-5,6-dihydro-β rings followed by the rearrangement of the epoxy

group into a 5-hydroxy-allenic end group.[12] Therefore, the capsoneoxanthin may be formed in two different ways from violaxanthin: (a) first, neoxanthin is formed, which transforms into capsoneoxanthin by pinacol rearrangement; (b) first, capsanthin 5,6-epoxide is formed by pinacol rearrangement and then the allenic end group is formed. Since capsoneoxanthin has never been detected in plants that contain capsanthin 5,6-epoxide in large amounts,[13–15] we assume that route (a) is more likely. The confirmation of this assumption demands further biochemical investigation.

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7. ^{1}H NMR (400 MHz, $CDCl_3$: δ (ppm) 0.83 (s, 3H, CH_3(16′)), 1.06 (s, 3H, CH_3(16)), 1.20 (s, 3H, CH_3(17′)), 1.32 (s, 3H, CH_3(17)), 1.33 (dd, 1H, H-2_{ax}), 1.34 (s, 3H, CH_3(18)), 1.36 (s, 3H, CH_3(18′)), 1.40 (dd, 1H, H-4_{ax}), 1.47 (dd, 1H, H-4′β), 1.70 (dd, 1H, H-2′β), 1.80 (s, 3H, CH_3(19)), 1.94 (dd, 1H, H-2_{eq}), 1.95 (s, 3H, CH_3(19′)), 1.97 (s, 6H, CH_3(20,20′)), 1.99 (dd, 1H, H-2′α), 2.26 (dd, 1H, H-4_{eq}), 2.95 (dd, J = 14.3, 8.4 Hz, 1H, H-4′α), 4.31 (m, 1H, H-3), 4.51 (m, 1H, H-3′), 6.03 (s, 1H, H-8), 6.11 (d, J = 11.5 Hz, 1H, H-10), 6.25 (d, J = 11.2 Hz, 1H, H-14), 6.34* (d, J = 15.2 Hz, 1H, H-12), 6.34* (d, J = 10.5 Hz, 1H, H-14′), 6.44 (d, J = 15.1 Hz, 1H, H-7′), 6.51 (d, J = 14.6 Hz, 1H, H-12′), 6.55 (d, 1H, H-10′), 6.57 (dd, 1H, H-11), 6.60 (dd, 1H, H-11′) 6.64 (m, 1H, H-15), 6.68 (m, 1H, H-15′), 7.32 (d, J = 15.1 Hz, 1H, H-8′); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 12.4 (CH_3(20,19′,20′)), 13.6 (CH_3(19)), 20.8 (CH_3(18′)), 24.7 (CH_3(17′)), 25.4 (CH_3(16′)), 28.9 (CH_3(17)), 31.0 (CH_3(18)), 31.8 (CH_3(16)), 44.9 (C(4′)), 48.5 (C(4)), 49.0 (C(2)), 50.4 (C(2′)), 64.0 (C(3)), 70.0 (C(3′)), 102.9 (C(8)), 120.6 (C(7′)), 128.1 (C(10)), 134.9 (C(14′)), 140.4 (C(10′)), 141.6 (C(12′)), 146.5 (C(8′)). *Assignment may be interchanged.
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