Unravelling the chemical property of the colouration bathochromic shift in the lobster carapace; a new crystal structure of unbound astaxanthin

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The colouration mechanism in the lobster carapace was revealed at 3.2Å resolution by a protein crystal structure of β-crustacyanin (Cianci et al 2002 PNAS). The crystals are a vivid blue colour. This structure suggested the candidate molecular parameters that are responsible for the bathochromic shift, which is most famously demonstrated via the colour change of lobsters on cooking, turning from blue/black to orange/red. The colour tuning parameters were proposed to include the following: firstly, the coplanarisation of the end rings with the polyene chain, increases the number of conjugated, alternating single and double bonds from 9 to 13; secondly, an electronic polarisation effect stemming from a histidine, found at one end of each of the bound astaxanthins, which is hydrogen bonded to an end ring keto oxygen. At the other end, the equivalent keto oxygen atoms are each hydrogen bonded to a bound water molecule; the keto and water oxygen atoms are a short distance apart (2.6(3) and 2.7(3)Å, respectively), which attracted attention in the protein structure analysis. The confidence however, in these two distances, at the 3.2 Å resolution of the analysis, was low. We have therefore determined a new crystal structure of unbound astaxanthin, which was crystallised by slow evaporation of a chloroform/hexane solution. These crystals are very thin, vivid orange/red plates, but were studied to standard small-molecule precision using a Mo Kα CCD APEX diffractometer. Interestingly, the astaxanthin crystal packing reveals a hydrogen bond between an end ring OH group and a neighbouring astaxanthin keto oxygen with a hydrogen bond distance of 2.786(5) Å. The details of the crystal structure at 0.84 Å are of course much more precise than the 3.2 Å protein crystal structure analysis. The comparison of the astaxanthins in these crystals will be presented.

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Reference

M Cianci, P J Rizkallah, A Olczak, J Raftery, N E Chayen, P F Zagalsky and J R Helliwell “The molecular basis of the coloration mechanism in lobster shell: β-crustacyanin at 3.2 A resolution” (2002) PNAS USA 99, 9795-9800.