s13.m35.o4 **Unravelling the chemical property of the colouration bathochromic shift in the lobster carapace; a new crystal structure of unbound astaxanthin**. Jennifer Coppin, John R. Helliwell and Madeleine Helliwell, *Department of Chemistry, University of Manchester, Manchester M13 9PL. E-mail: madeleine.helliwell@man.ac.uk*

Keywords: Astaxanthin; Crustacyanin; Bathochromic Shift

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

[1] 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.

s13.m35.o5 **From dihydroxyacetone (DHA) to dihydroxyacetone phosphate (DHAP) – solving the problem by the use of X-ray crystallography**. Katarzyna Slepokura and Tadeusz Lis, *Faculty of Chemistry, The University, 14. F. Joliot-Curie, Wroclaw, Poland. E-mail: slep@o2.pl*

Keywords: dihydroxyacetone, DHA; dihydroxyacetone phosphate, DHAP; chemical synthesis; crystal structures

The biological role of DHA (a ketotriose representing the carbohydrates family) and DHAP (its phosphate ester, one of the most important biochemical intermediates that acts in the main metabolic pathways, such as glycolysis, the substrate for many enzymes, including triosephosphate isomerase (TIM) and several aldolases) has been well known for many years. Nevertheless, the molecular structure of neither DHA nor DHAP has not been described in the literature up to this day. In addition, only few synthetic methods yielding DHAP have been reported, most of them being long, expensive and inefficient. The results of structural investigations on the chosen [1], slightly modified chemical pathway leading from DHA to DHAP (Fig. 1) will be presented.

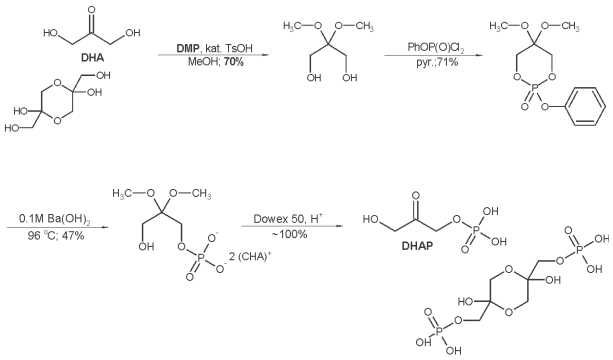

Fig. 1. Chemical pathway scheme leading from DHA to DHAP [1].

The structures of all of the intermediates and its derivatives have been determined by the use of crystallographic methods. Three different crystalline forms of DHA dimer (**I**) - (**III**), DHA monomer (**IV**) and its calcium chloride complexes (**V**), (**VI**), its dimethyl acetal (**VII**), five different dihydroxyacetone phosphate dimethyl acetal salts along with the related cyclic form (**VIII**) - (**XIII**), and finally DHAP in dimeric as well as monomeric form (**XIV**), (**XV**) will be presented. The characteristic of DHA and DHAP (Fig. 2) is their planarity; the DHA molecules in all (**IV**) - (**VI**) as well as DHAP anion in (**XV**) are in an extended conformation.

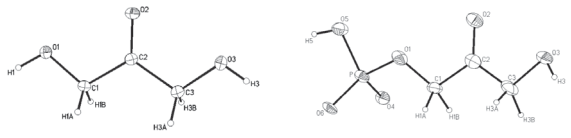

Fig. 2. DHA molecule in (VI) and DHAP anion in (XV).

Additional solution structure investigations (NMR techniques) concerning DHAP have revealed existence of its two monomeric forms: free carbonyl and hydrated monomer (gem-diol) in a ratio 1:1, which is consistent with similar results (4:1 ratio) reported for dihydroxyacetone by Davis in 1973 [2].

[1] Ferroni, E. L., DiTella, V., Ghanayem, N., Jeske, R., Jodlowski, C., O'Connell, M., Styrsky, J., Svoboda, R., Venkataraman, A., Winkler, B. M. *J. Org. Chem*., **64** (1999) 4943.
[2] Davis, L. *Bioorganic Chemistry*, **2** (1973) 197.