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

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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.

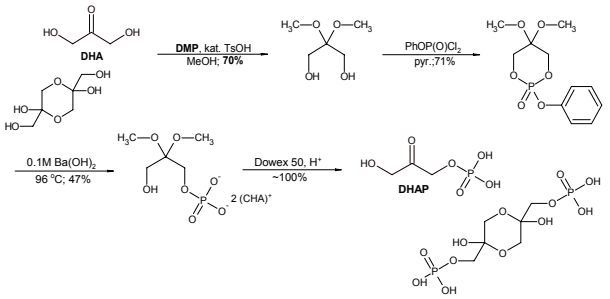

Fig. 1. Chemical pathway scheme leading from DHA to DHAP [1].

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.

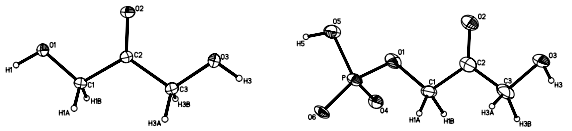

Fig. 2. DHA molecule in (**VI**) and DHAP anion in (**XV**).

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.