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Most of nucleoside 5'-monophosphates have been extensively investigated as regards their structure for long, but potassium salts of them have never been studied by the use of X-ray crystallography. The results of structural investigations on five mono- and dipotassium salts of two purine [ $K_2(AMP)6H_2O$ ,  $K(IMP)3H_2O$ ] and two pyrimidine [ $K_2(CMP)6.25H_2O$ ,  $K(UMP)$ ,  $K_2(UMP)5H_2O$ ] ribonucleotides will be presented. The  $K^+$  salts crystallize with  $Z' = 1-4$  for the respective crystal. In all the mono-/dianions, the orientation of the base with respect to the sugar ring is *anti*, which is typical for nucleotides. The ribose rings in AMP and UMP salts exist in ideal envelope conformations:  ${}^2E$  in two dianions in  $K_2(AMP)6H_2O$  and two dianions in  $K_2(UMP)5H_2O$ , and  ${}^3E$  in the monoanion in  $K(UMP)$ . The sugar rings in the remaining crystals are slightly deformed from the ideal pucker, with the nearest descriptors being:  ${}^3T_2$  for the IMP monoanion,  ${}^2T_1$  for two CMP dianions and  ${}^3T_4$ ,  ${}^2E$  for two remaining CMP dianions. The orientation of the phosphate relative to the ribose ring is the same in all the anions: *gauche-gauche*, which is characteristic of the 5'-nucleotides. The arrangement of the terminal phosphate atoms relative to the ester C5' is *antiperiplanar (ap)* for one of O atoms and *+/-synclinal (+/-sc)* for the others in most of the presented nucleotides. However the phosphate group in the IMP monoanion is disordered and exists in two orientations: typical *ap/sc* and quite uncommon *sp/ac*.

Keywords: nucleotides, ribonucleotides, biological compounds

## P05.05.08

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### Sesquiterpene lactones isolated from a medicinal plant of the Venezuelan Andes

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Sesquiterpene lactones are perhaps the most studied members of the terpenes because a large number of them exhibit pharmaceutical activity. The structures of two sesquiterpene lactones, Tenuline and Gaillardiline, isolated from a medicinal plant of the Venezuelan Andes (*Ambrosia cumanensis*) will be presented in this contribution. Tenuline,  $C_{17}H_{22}O_5 \cdot 2(H_2O)$ , crystallizes in the orthorhombic system, space group  $P2_12_12_1$ , with unit cell parameters  $a=6.9501(2)$ ,  $b=9.5145(3)$ , and  $c=25.7739(8)$  Å,  $V=1704.34(9)$  Å<sup>3</sup>,  $Z=4$ ,  $d_c=1.334$  g cm<sup>-3</sup>. Due to the presence of the water molecules in the structure, there is an extensive hydrogen bonding network which helps stabilize the structure. There are eight inter- and one intra-molecular hydrogen bond. Gaillardiline,  $C_{17}H_{22}O_6$ , crystallizes in  $P2_12_12_1$  with unit cell parameters  $a=9.0749(3)$ ,  $b=11.1830(3)$ ,  $c=15.8804(4)$  Å,  $V=1611.62(8)$  Å<sup>3</sup>,  $Z=4$ ,  $d_c=1.329$  g cm<sup>-3</sup>. Three inter- and four intramolecular hydrogen bonds help to stabilize the structure. Both hydrogen bond networks can be described using graph set theory. They will be discussed in detail. We thank R. Benson (Rigaku-USA), for support with data collection using Cu radiation. This work was funded by FONACIT-Venezuela, through grant LAB-97000821.

Keywords: natural products, sesquiterpene lactones, crystal structure

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### Organic two-photon absorbing materials for technological applications and photodynamic therapy

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Two-photon absorbing (TPA) chromophores are used in the technology for three-dimensional microfabrication by lithographic process and in biomedical applications as fluorescent markers for TPA microscopy and as photosensitizers in PTA photodynamic therapy. Advantage of TPA chromophores in comparison with conventional one-photon absorbing chromophores is an opportunity to achieve a very high spatial resolution in three dimensions and so treat tumors without damage to neighboring healthy organs. We studied structures of a large series of substituted benzylidenepiperidones, organic chromophores with general formula Donor- $\pi$ -bridge-Acceptor- $\pi$ -bridge-Donor. Structure – properties relations between geometric and spectroscopic characteristics of materials, important for their PDT applications, have been established. Dark toxicity and toxicity under irradiation have been characterized and discussed in connection with spectroscopic properties of materials.

Keywords: two-photon absorbing materials, photodynamic therapy, spectroscopy

## P05.07.10

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### The structure of water nanopipe, a hollow-type water nanowire, in crystal host

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One-dimensional (1D) water nanostructures are important for better understanding the structure and behavior of water molecules at the atomic level. Previously we reported the first water nanowire in the crystal structure of L-tryptophan pyridoxal-5-phosphate Schiff base, obtained from its aqueous solution [1,2]. Here, we report the second water nanowire, called water nanopipe, in the crystal obtained from another batch of aqueous solution of the Schiff base. This nanopipe is a hollow-wire type nanowire, where the diameter and unit length (equals to the length of c-axis) are 1.649 nm and 0.473 nm. The structure is constructed in such a way that five water molecules form a small cluster unit, and three of the small units are linked around a three-fold axis to form a large cluster unit consisting of 15 water molecules. These large units are then piled up by nine hydrogen bonds parallel to c-direction and form an infinite water nanopipe. In this structure, seven kinds of hydrogen bonds are formed by five independent water molecules: the O--O distances are 0.246, 0.247, 0.272, 0.281, 0.290, 0.293 and 0.295 nm and the hydrogen-bonded O-O-O angles range from 82 to 135°. This nanopipe structure is assumed to be much more stable than the nanowire structure, because the more hydrogen bonds are formed along to the piling-direction in the nanopipe than the nanowire, and the very long needle crystals up to 2.6 cm are obtained for the nanopipe structure. Therefore, it would be considered that the present nanopipe structure provides a structural scaffold between the nanoworld (nm) and the real world (cm) in the

water structure.

References

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Keywords: water, nanopipe, nanowire

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### H-bonds in andrographolide and related molecules: Neutron diffraction, database and modeling studies

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The biologically active natural product andrographolide has OH and CH<sub>2</sub>OH groups at adjacent positions on a decalin ring. Our neutron diffraction study confirms that the OH group is the donor and O(H)CH<sub>2</sub> the acceptor in an intramolecular hydrogen bond (IHB) with H ··· O 1.743(6) Å and O-H ··· O 153.9(5)°, the latter group hydrogen bonding to the OH group of a nearby molecule. A priori this scheme seems preferable since with two rotatable bonds CH<sub>2</sub>OH should adapt better than OH to the vagaries of crystal packing. However, an X-ray study of a derivative acetylated at a remote OH group showed the reverse pattern. A CSD search with normalized H atoms for cyclohexane rings with adjacent OH and CH<sub>2</sub>OH groups gave 34 matching fragments: 7 with OH ··· O(H)CH<sub>2</sub> ≤ 2.3 Å, 13 with CH<sub>2</sub>OH ··· OH ≤ 2.3 Å, the remainder with weaker or no IHB. The former class has 'better' IHB with <H ··· O> 1.82 Å and <O-H ··· O> 142° vs. 1.90 Å and 137°, yet is less numerous. Molecular dynamics suggests a swap to the former when cyclohexane changes to decalin. Cluster analysis with dSNAP classifies mainly IHB type but also substituent location. Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357, and the Malaysian Ministry of Science, Technology and Innovation (MOSTI) grant no. 02-01-04-SF0089.

Keywords: neutron diffraction, hydrogen bonding, natural products

## P06.01.01

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### Crystal structure of trehalose dihydrate by X-ray and neutron diffraction experiments

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Trehalose is a non-reducing disaccharide that is a frequently synthesized in living organisms as an intracellular protectant or co-protectant against harsh conditions, permitting organisms to survive dehydration or freezing. As this characteristic property is still open to argument, a large number of studies on biopreservation have been performed. However, there are few reports on the crystallographic investigation for trehalose. We have, therefore, tried to determine

both the crystal structure and the electron density distribution (EDD) of trehalose dihydrate using the single-crystal X-ray and neutron diffraction data for understanding of the structural characteristics. The crystal structure of trehalose dihydrate was refined with the data at room temperature. Furthermore, in order to reduce an influence of atomic displacement parameters on the structure refinement, X-ray diffraction intensity has been measured at low temperature. Both the refinement and MEM analysis were performed for obtaining the EDD again. From the results, the covalent bonding was confirmed to exist between the trehalose and the internal water. The EDD, thus obtained, was compared with that calculated using the full-potential linealized augmented plane wave (FLAPW) method.

Keywords: absolute structure determination, electron density distribution, trehalose dihydrate

## P06.01.02

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### Temperature-dependent structural change of trehalose dihydrate and anhydrate crystals

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Thermal analysis method is widely used in order to determine the phase transition temperature for the easier technique, but it is difficult to obtain a detailed information of the temperature. On the other hand, *in-situ* high-temperature powder X-ray diffraction technique is a powerful tool to investigate a detailed structural change. We have, therefore, determined both the crystal structures and the phase transition temperature of trehalose dihydrate and anhydrate crystals using the high-temperature *in situ* powder X-ray diffraction data and the detailed temperature-dependent structural change was investigated. Trehalose anhydrate was obtained by dehydrating from trehalose dihydrate. The melting and crystal-amorphous phase transition peaks of trehalose anhydrate by DSC and TG-DTA were confirmed that it is around 453K. The crystal structure of trehalose anhydrate was refined with the use of powder X-ray diffraction data between 373K and 467K. From this result, trehalose anhydrate have crystal-amorphous phase transition at 461K. For trehalose dihydrate, the same experiment was performed and crystal-amorphous phase transition temperature was confirmed to be around 353K. The structural parameters, i.e. changes of atomic distance in trehalose molecule, were obtained at this temperature. The result, thus obtained, was compared with that calculated using molecular dynamics method.

Keywords: Rietveld structural refinement, *in-situ* powder diffraction, phase transitions

## P06.01.03

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### HTXRD and XRD-DSC study of crystalline-noncrystalline phase transition of sucrose crystals

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