

Chimia 54 (2000) 531–533
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ISSN 0009–4293

Silver and Bronze Medals for Switzerland at the 32nd International Chemistry Olympiad

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Keywords: International Chemistry Olympiad · Swiss students

The 32nd International Chemistry Olympiad was held in Copenhagen, 2–10 July, 2000. 53 countries participated with usually four candidates per country (sometimes less, as there were 208 candidates in all).

The students had a practical examination of 5 h, where they had to synthesize one organic and one inorganic compound, and also perform titrations. The theoretical examination, also 5 h, consisted of five tasks in widely spread fields. A detailed description of these tasks is reported at the end of this article.

The best students received gold, silver and bronze medals. Switzerland won two medals, thanks to Daniel Torricelli from Kloten (silver) and Jean Garnier from Lausanne (bronze). This is a better result than in 1999, where our country won only one medal. A total of 23 gold, 44 silver and 66 bronze medals was awarded in Copenhagen. The best student came from

the United States of America, followed by two students from China. Russia had the best overall score with four gold medals.

The students had also the opportunity of visiting Copenhagen and its surroundings, several castles, scientific exhibitions and lectures, and to compete in an orienteering race, in which the winning team included our Swiss silver medallist, Daniel Torricelli.

The Swiss team was trained for one week in the Gymnase de Chamblandes, Pully VD. After a theoretical examination the four students selected were:

- Juliette Ben Arous, Gymnase de la Cité, Lausanne
- Jean Garnier, Gymnase de la Cité, Lausanne (bronze)
- Dominic Rossi, Gymnase A. Piccard, Lausanne
- Daniel Torricelli, Kantonsschule Oerlikon (silver).

The mentors were Dr. Jochen Müller (Zürich) and Dr. Blenda Weibel (Lausanne).

Furthermore Switzerland has presented its candidature to host an Olympiad in 2004. This project was accepted by the International Jury in Copenhagen. A committee is already at work in our country to start up this huge project and put it on the rails.

The next Olympiads will be 2001 in India, 2002 in the Netherlands, 2003 in Greece, 2004 in Switzerland, 2005 in Chinese Taipei, 2006 in Korea, and 2007 in Turkey.

We would like to express our gratitude to the New Swiss Chemical Society, and especially to Prof. Dr. Reinhard Neier, whose continuous support has allowed our team to take part to these Olympiads for many years.



From left to right: Daniel Torricelli (silver), Dominic Rossi, Jean Garnier (bronze), Juliette Ben Arous

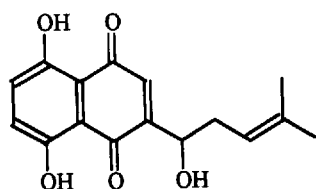


From left to right: Daniel Torricelli (silver), Dr. Jochen Müller, Juliette Ben Arous, Dominic Rossi, Dr. Blenda Weibel, Jean Garnier (bronze), the interpreter

Tasks from the Theoretical Examination

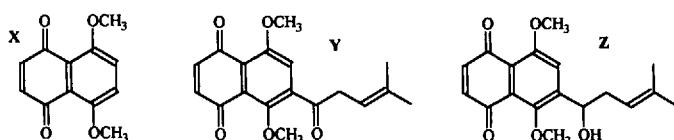
Problem 1 (10 Points)

Shikonin is a natural compound extracted from the roots of an exotic plant. It has the following structure:



- How many stereoisomers of Shikonin are possible?
- Do all stereoisomers of Shikonin have the same melting point?

The following sequence **X-Y-Z** is part of a synthetic route to Shikonin, where a reagent **A** and a catalyst **B** are needed to go from **X** to **Y**, and a reagent **C** is needed to go from **Y** to **Z**.

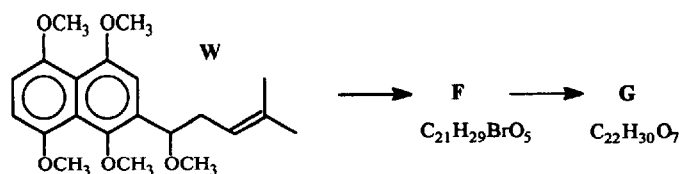


- Draw the formula of reagent **A**.
- Indicate the correct IUPAC name for reagent **A**.
- Write the molecular formula of reagent **C**.

Shikonin reacts with SOCl_2 to form **D** = $\text{C}_{16}\text{H}_{15}\text{ClO}_4$. Treated with KOH in ethanol, **D** is transformed into **E** = $\text{C}_{16}\text{H}_{14}\text{O}_4$.

- What is the formula of compound **E**?
- How many stereoisomers of **E** are possible?

Another route to Shikonin analogues is the following:

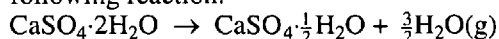


Transforming **W** into **F** requires HBr in a polar solvent. Transforming **F** into **G** requires Mg in diethyl ether, adding CO_2 , then using aq. HCl .

- Draw the structural formula of compound **F** and **G**.

Problem 2 (10 Points)

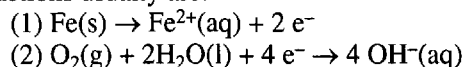
- Calculate ΔH for the transformation of 1.00 kg of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to plaster $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ according to the following reaction:



The following ΔH_f data (in kJ/mol , and at 25°C and 1 bar) apply to gypsum, plaster and $\text{H}_2\text{O}(\text{g})$ respectively: -2021 , -1575 , -241.8 . And the corresponding entropies are: 194.0 , 130.5 and $188.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

- Calculate the equilibrium pressure of water vapor in a closed vessel containing gypsum, plaster and water vapor at 25°C .
- Calculate the temperature at which the equilibrium water vapor pressure is 1 bar, assuming ΔH and ΔS are temperature independent.

In the formation of rust on iron surfaces the initial electrode reactions usually are:



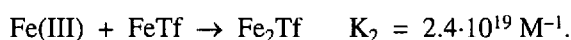
Corresponding standard electrode potentials at 25°C are: $E_1 = -0.44 \text{ V}$, $E_2 = +0.40 \text{ V}$.

- Calculate the standard cell voltage of the cell represented by the following diagram:
 $\text{Fe}(\text{s}) / \text{Fe}^{2+} // (\text{OH}^-(\text{aq}), \text{O}_2(\text{g}) / \text{Pt}$
- Write down the overall reaction which takes place during the discharge.
- Calculate the equilibrium constant at 25°C for the cell reaction.
- The cell produces 0.12 A. What is the mass of Fe converted in Fe^{2+} in 24 hours?
- Calculate E for the cell at 25°C with the following conditions: $[\text{Fe}^{2+}] = 0.015 \text{ M}$, $p(\text{O}_2) = 0.700 \text{ bar}$, and $\text{pH} = 9.00$ in the right-hand half-cell.

Problem 3 (9 Points)

- Draw the *cis*- and *trans*-structures of *cis*- and *trans* diamminedichloroplatinum(II), which is a square-planar complex.
- Several ionic compounds have the empirical formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Write the molecular formulas for all ionic compounds containing an anion and a cation each made of square-planar Pt(II) complexes.
- How many 5d electrons does the Pt(II) ion have?
- Which of the five 5d electrons attains the highest energy in the general case of a square-planar Pt(II) complex? To solve this problem, it is assumed that the valence d-orbital energy splitting diagram for a square-planar complex is derived from that of an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the z-axis vanish, while the bonds to the four remaining ligands on x- and y-axes become stronger.

Serum transferrin (abbreviated Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 corresponding to the reactions:



Two possible FeTf isomers are known, which will be called FeTf' and FeTf'' . Their relative abundance at equilibrium is given by the constant K .

$$K = [\text{FeTf}''] / [\text{FeTf}'] = 5.9$$

In the diferric protein Fe_2Tf , the two iron(III) ions are bound at two similar but non-identical sites.

- Calculate the values of the four constants K_1' , K_1'' , K_2' and K_2'' given by:

$$K_1' = \frac{[\text{FeTf}]}{[\text{Fe(III)}][\text{Tf}]} \quad K_1'' = \frac{[\text{FeTf}']}{[\text{Fe(III)}][\text{Tf}']}$$

$$K_2' = \frac{[\text{Fe}_2\text{Tf}]}{[\text{Fe(III)}][\text{FeTf}]} \quad K_2'' = \frac{[\text{Fe}_2\text{Tf}']}{[\text{Fe(III)}][\text{FeTf}']}$$

3.6. In each binding site the bound iron(III) ion is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a CO_3^{2-} ion coordinate to the metal and the following amino acid side chains from the protein structure also coordinate to the iron(III) ion with one donor atom each: one aspartate, one histidine, and two tyrosine residues. What is the total number of oxygen donor atoms that surround the iron(III) ion in transferrin?

Problem 4 (10 Points)

A naturally occurring product **A** has the following composition in mass :

C: 63.2% H: 5.3% O: 31.5%

- 4.1. What is the empirical formula of **A**?
- 4.2. The mass spectrum has only two important peaks at 151 and 152, and very small peaks at 81, 109, 123 and 137. What is the molecular formula for **A**?
- 4.3. If a solution of **A** in ether is shaken with an aq. soln. of NaOH, no **A** remains in the ether phase. But if NaHCO_3 is used instead of NaOH, all **A** remains in the ether phase. Is **A** an acid, an alcohol, an aldehyde, an ester, an ether, a ketone or a phenol?
- 4.4. Compound **A** reacts with Tollens' reagent $\text{Ag}(\text{NH}_3)_2^+$ producing a silver mirror. Which functional group is in **A**?

The NMR spectrum of **A** displays five signals: 1; 9.8 ppm (s, integral = 0.94). 2; 7.4 ppm (sextett, integral = 1.91). 3; 7.0 ppm (d, integral = 0.93). 4; 6.3 ppm (s, integral = 0.94). 5; 3.9 ppm (s, integral = 3.10). A table of chemical shifts is given in an appendix.

- 4.5. The signal at 6.3 ppm disappears when a drop of D_2O is added. What does it mean? Hydrolysis? Exchange of H from a CH bond, or from a OH bond? Dilution effect?
- 4.6. The same signal moves to a lower ppm value upon dilution with CDCl_3 . Which of the following does this indicate? Indicate the true statements (more than one). a) Increased H bonding. b) Decrease in H bonding. c) Intermolecular H bonding. d) Intramolecular H-bonding. e) No H bonding.
- 4.7. Draw the four possible structures for **A**.
- 4.8. What are the fragments lost corresponding to the peaks at 137 and 123 in the MS?
- 4.9. Two isomers have a pK_a value lower than the others. Write their formulas.

Problem 5 (10 Points)

DNA is composed of 2'-deoxy-nucleotides carrying the bases adenine (A), guanine(G), cytosine(C), and thymine(T). The molar masses of some 2'-deoxy-nucleotide-5'-triphosphates dNTP are: dATP 487; dGTP: 503; dCTP: 464; dTTP: 478.

- 5.1. Calculate the molar mass of a double-stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat-sta-

ble DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. The number of double-stranded DNA copies doubles in each cycle.

- 5.2. Calculate the mass of the DNA obtained if 30 cycles are performed starting from a single double-stranded DNA molecule.

Treated by an enzyme called PNK, DNA can be bound to a phosphate group and yields the molecule called 5'-P-DNA. A carrier-free aq. soln. of 5'-P-DNA contains the β -emitter P-32 with a specific activity of 10 Ci/mmol, or $3.7 \cdot 10^{11}$ Bq/mmol. Then 10 μl of this soln. is taken for analysis. After 37 d, it emits 40 000 β -particles per sec.

- 5.3. What is the concentration of the 5'-P-DNA soln. if P-32 has a half-life of 14.2 d?

The production of this 5'-P-DNA (called labeling) is monitored continuously in a mixture of DNA + PNK by isolating it and measuring the β -particle emission. In a given experiment, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant of 0.05 s^{-1} , and a molar mass of 34620 g mol^{-1} .

- 5.4. What is the concentration in mg/ml of PNK in the experimental mixture?

All aromatic amino acids (tyrosine, phenylalanine, tryptophane) absorb UV light at 280 nm. Their molar absorptivity ϵ is 1400, 5, and $5600 \text{ M}^{-1}\text{cm}^{-1}$, respectively. These values are not changed if these amino acids are included in a protein like PNK, which contains 14 tyrosines and 9 phenylalanines.

- 5.5. Calculate the number of tryptophane residues in a PNK molecule, if the absorbance of a $10 \mu\text{M}$ solution of PNK is 0.644 at 280 nm with a 1.00 cm light path.

Practical Tasks

The practical tasks will not be described in detail. The candidate had first to synthesize an unusual complex of manganese(III): $\text{K}_3\text{Mn}(\text{C}_2\text{O}_4)_3$. Then they had to determine both its oxidizing power with KI, and its reducing power with KMnO_4 . Simultaneously the candidates had to synthesize the methyl ester of the amino acid (S)-serin using a microscale technique with 0.2 g (S)-serin and 0.52 g SOCl_2 dissolved in 10 ml of methyl *tert.*-butyl-ether.

Received: August 10, 2000

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