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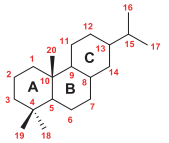
ABIETANE DITERPENOIDS AS POTENTIAL DRUGS

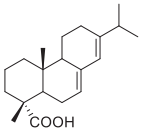
Abietanes are naturally occurring diterpenoids that have been isolated from several terrestrial plant families including Lamiaceae (Labiatae), Asteraceae, Celastraceae, and Boraginaceae, and resins from conifers belonging to the families Cupressaceae, Pinaceae, Podocarpaceae, Phyllocladaceae, and Araucariaceae.

Secondary metabolites of plants can be classified, namely as terpenoids and steroids, flavonoids and other phenolics, and alkaloids, which all play an important role in their defense mechanisms, such as fighting with herbivores, pests, and pathogens as well as other types of external damage. As one of the secondary metabolites of plants, terpenoids are composed of isoprene (*2-methyl-1,3-butadiene*) units. The name "terpene" is derived from the word "turpentine". Each isoprene unit also called a "C5 building block" or hemi-terpene; they are linked to form terpenes in "head-to-tail" fashion, in general. Therefore, monoterpenes are formed from 2 isoprene units (10 C's), sesquiterpenes from 3 units (15 C's), diterpenes from 4 units (20 C's), and sesterterpenes from 5 units (25 C's), while triterpenes are from 6 units (30 C's) and tetraterpenes from 8 units (40 C's).

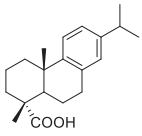
Mono- and sesquiterpenoids are the main constituents of the essential oils of all plants and flowers and they give them their special smell and taste. Diterpenoids are composed of four isoprene units with a core molecular formula $C_{20}H_{32}$to form different skeletons, such as abietane, kaurane, atisane, labdane, jatrophane, tigliane, lathyrane, or taxane.



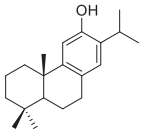
Abietane skeleton



Abietic acid



Dehydroabietic acid



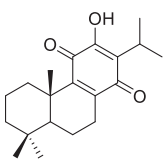
Ferruginol

Abietane diterpenoids have three six-membered cyclic rings (*trans*-fused A-B, and *trans*-fused B-C rings) with an isopropyl side chain attached to C-13 on ring C. A simple example of them is abietic acid (7,13-abietadien-18-oic acid), and dehydroabietic acid, which has an aromatic ring C, previously obtained during chemical studies starting from abietic acid. Another simple abietane diterpene with the aromatic ring C is ferruginol, first isolated in 1939 from the resin of the miro tree (*Podocarpus ferrugineus*) endemic to New Zealand [1].

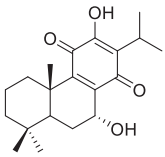
Aromatic abietanes comprise the largest group of naturally occurring abietanes [1] and are the main secondary metabolites of the *Salvia* L. (sage) plants belonging to the family Lamiaceae. The genus *Salvia* is represented by over 900 species throughout the world, and the best known *Salvia* species are *S. miltiorrhiza* (Danshen or Tanshen) in China and other Asian countries, *S. officinalis* L. in Europe (sage), and *S. fruticosa* Mill. (syn: *S. triloba* L.) in Mediterranean countries, and *S. divinorum* L., a hallucinogenic species, whose origin dates back to the Mazatec hallucinogenic sage. Most *Salvia* species are rich in abietane diterpenoids, while *S. divinorum* is rich in neo-clerodane diterpenoids. In Turkey, *Salvia* species are represented by over 100 species (114 taxa), and half of them are endemic to Anatolia (Asian part of Turkey).

During our group studies on *Salvia* species by Prof. Ulubelen and by Prof. Topcu, over 140 abietane diterpenoids were isolated [2,7], at least half of them being new, and most of them have an aromatic ring C. Their structures were elucidated based on 1D- and 2D-NMR and mass spectroscopic analyses as well as UV and IR spectrophotometric measurements.

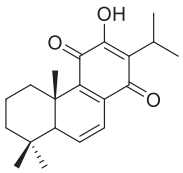
Some abietane-type diterpenoids have a *para*-quinone C ring, such as royleanone and horminone, or an *ortho*-quinone C ring, such as miltirone [8], but the last of these was a norditerpene with 19 C atoms.



Royleanone



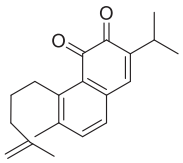
Horminone



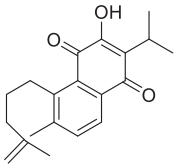
6,7-Dehydroroyleanone

Furthermore, some abietanes contain an enone group in ring B conjugated to the aromatic ring C such as taxodione, salvinolone, and 6-hydroxysalvinolone.

Some *Salvia* species afforded abietane diterpenoids that have opened ring A, which are called seco-abietanes, such as aethiopinone and salvipisone [2,8].

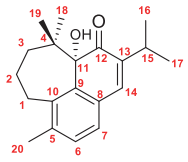


Aethiopinone

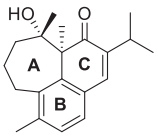


Salvipisone

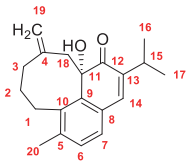
The most interesting re-arranged abietanes were obtained from endemic Anatolian *Salvia* species, such as *S. microstegia* Boiss. et Bal. growing in the Binboğa Mountains (Turkey), which afforded a rearranged tricyclic abietane diterpene. Its structure was elucidated by a series of NMR techniques, such as ^{1}H and ^{13}C NMR, COSY and 1D-NOE and SINEPT experiments as well as HRMS analysis. Examination of its unusual carbon skeleton suggested that this compound might be derived biogenetically from regular abietane diterpene having a three six-membered C skeleton by ring A cleavage between C-4 and C-5, followed by recyclization of C-4 to C-11. Therefore, the final product, named microstegiol, with a seven-membered ring A, is optically active, suggesting that the rearrangement is under enzymatic control, and it was found to be active against P-388 lymphocytic leukemia cells (ED_{50} = 3.0 μg/mL) [3]. Total synthesis of microstegiol was carried out by Taj and Green and published in 2010 [9].



Microstegiol

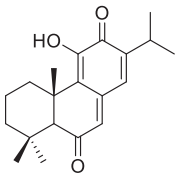


Salvibretol

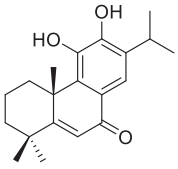


Candidissiol

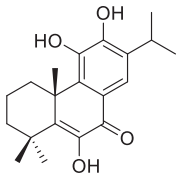
Another endemic *Salvia* species, *S. candidissima*, also afforded a re-arranged abietane with an eight-membered ring A, which is very unusual for natural compounds, and its structure was identified by extensive NMR techniques running 1D and 2D NMR experiments and named candidissiol [4].



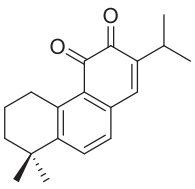
Taxodione



Salvinolone

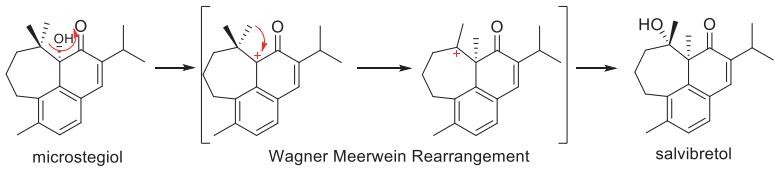


6-Hydroxysalvinolone

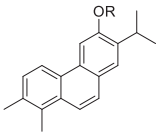


Miltirone

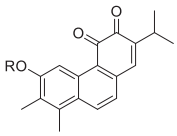
Salvibretol and its natural derivatives 1-oxosalvibretol and 3-oxosalvibretol were isolated first from *S. montbretii* [5], and later from a few other *Salvia* species [2,5], and their structure analyses were elucidated by sophisticated NMR and mass techniques. The formation of salvibretol [5] from microstegiol through Wagner–Meerwein rearrangement is seen below, which is a very common carbocation reaction in natural products.



Multicaulins were isolated as a series of fully aromatic abietane diterpenoids; their skeleton has 19 C atoms since they were converted into norabietanes from abietanes and they showed very strong antituberculous activity against *Mycobacterium tuberculosis* [2,10].



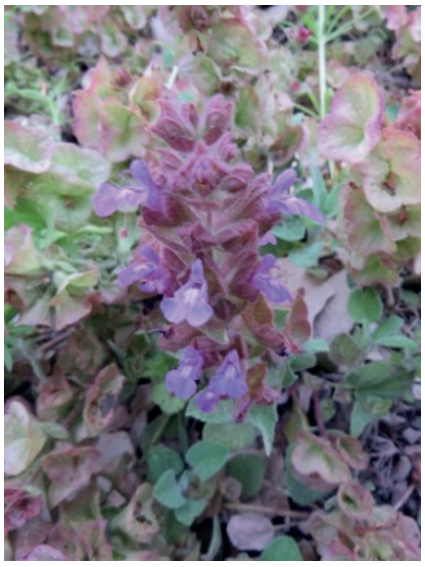
R= CH_3: Multicaulin
R= H: Demethylmulticaulin



R= CH_3: Multiorthoquinone
R= H: Demethyl-multiorthoquinone

Salvia microstegia Boiss et bal.

Salvia montbretii Benth.



Salvia multicaulis Vahl

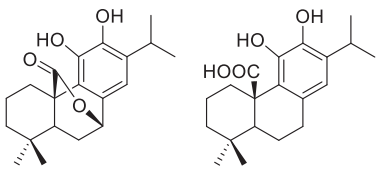
Salvia triloba L. f.

Salvia triloba L. with 3 lobe leaf

Salvia officinalis L.

It is notable that the extracts of *Salvia* roots were found to be rich in diterpenoids, particularly abietane diterpenoids, while their triterpenoids were isolated from the aerial parts rather than other parts.

S. fruticosa Mill., also named *S. triloba* due to its leaves with 3 lobes, Mediterranean sage, although Greek people call it Greek sage, Dalmatian people Dalmatian Sage Lebanon people Lebanese sage, and Turkish people Turkish sage. Its phytochemical structure [2] is fairly similar to that of European sage, *S. officinalis*; the main difference is observed in their essential oil. *S. triloba* contains almost no thujone, while *S. officinalis* is rich in thujone. Due to the presence of thujone, the European Medicines Agency (EMA) allows max. 5 mg/day thujone in medicinal plant products, such as *S. officinalis* essential oil. Therefore, *S. triloba* is much more preferable and valuable in terms of its essential oil. Both species contain strong antioxidant abietane diterpenoids, and the strongest ones are carnosol and carnosic acid. Carnosol protets us against narrowing of the cerebral arteries carrying blood to the brain. Carnosic acid increases the body's production of glutathione, which is one of the most important antioxidants, helping to protect the brain from free radical damage.



Carnosol Carnosic acid

Therefore, aromatic abietanes are strong antioxidant, and some of them might be used in neuroprotective and cardioprotective agents, such as carnosol and carnosic acid. Abietanes having ring C conjugated with enone or enol moiety on ring B, particularly such as taxodione and 6-hydroxysalvinolone, exhibited very strong cytotoxic activity against a series of cancer cell lines [2]. Thus, the potential impact of abietanes in the discovery of therapeutic drugs should be considered.

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Gülaçtı Topçu

MALATYA APRICOT

Flowering period of apricot

Apricot on the branch.

Dried apricot.

Historical Perspective

Apricot (*Prunus armeniaca* L.) is a plant whose homeland is Central Asia and Western China. It is cultivated in regions with a temperate climate zone from the Mediterranean to Australia. According to historical sources, it can be produced in many countries including Turkistan, Central Asia, and Western China. Apricots were known and cultivated in this region 5000 years ago. It was brought to Anatolia in the 1st century during the expeditions of Alexander the Great. It has become the second homeland of the apricot, as the climate and soil are suitable for its cultivation [1].

History of the Apricot in Malatya

The first written records on apricot in Malatya are from 1655. The famous traveler Evliya Çelebi[1], who came to Malatya, mentioned about 7800 orchards and 7 apricot varieties in Malatya where 53 thousand people lived. Çelebi also wrote that Malatya had apricots that were "red, yellow, white, juicy, and succulent" and that when someone brought them home from the garden, they had no choice but to run to keep them fresh. More importantly, he stated that unimaginable amounts of dried sheets of pulp were made from the heaps of apricots, loaded onto wagons, and transported to other countries [2].

Apricot Varieties Grown in Malatya

Approximately 90-95% of the apricot orchards in the region have been established with dried apricot varieties. While 73% of the cultivated apricot varieties are Hacıhaliloğlu, 17% are Kabaaşı, and the rest are Soğancı, Hasanbey, Çataloğlu, and zerdali (less than 1%) trees [2].

Agriculture and Production

In 2017, 536 thousand hectares of land worldwide was used for apricot production and 23.3% of this was in Turkey. Global fresh apricot production was 4.3 million tons in 2017. Most of the fresh apricot production in the world was in Turkey, with 985 thousand tons. According to 2018 data, Turkey exports annually 71 thousand tons of apricots and ranks third in exports worldwide. A total of 120 thousand tons of dried apricot exports were reported worldwide, with 94 thousand tons (78.2%) from Turkey. An important part of the produced apricot is considered dried apricot. Turkey is a leader in dried apricot production, followed by Spain with 4.2% and Kirghizstan with 3.4%. With the many advantages of its special ecological conditions, Malatya Province ranks first in production. Although the production of dried varieties is at

1 For further information about the most famous Ottoman traveler of the 17th century, see: https://en.wikipedia.org/wiki/Evliya_%C3%87elebi

the forefront in this country, most of the apricots produced in the world are for daily consumption [3,4].

Apricot Production

Approximately 770 thousand tons of apricot including zerdali species were produced last year in Turkey. Malatya has a special position in Turkey with 401 thousand tons of apricot, which is 52.1% of the total production [5]. Apricot fruit has become indispensable for Malatya due to its production amount and its contribution to the economy [6].

Medicine

Various mechanisms in the human body keep the oxidant and antioxidant defense mechanisms in balance. Some of these are healthy nutrition and dietary antioxidants.

The most prominent representatives of dietary antioxidants are carotenoids, ascorbate, tocopherols, and flavonoids [8]. According to the recent literature, apricot has significant antioxidant potential due to its content such as vitamins A and C and some polyphenols like beta carotene [9].

Nutritional Potential

Apricot is a fruit rich in carbohydrates, fiber, minerals, and vitamins among the hard fruits (Table 1) (10). It contains many bioactive phytochemicals, that is, polyphenols and carotenoids that have certain roles in the biological system and are effective in preventing oxidative stress damage [11]. These compounds also give the plant tissue colors (red, blue, and purple) and thus greatly contribute to the visual quality of the fruit [12]. Apricot also contains a reasonable amount of dietary fiber ranging from 1.5 to 2.4 g/100 g on a fresh weight basis [13]. It also contains various amounts of essential minerals. The main elements are potassium, phosphate, calcium, magnesium, iron, and selenium [14]. Sodium, manganese, zinc, and copper are also found in small quantities [15]. Similarly, the vitamins found in apricot include provitamin A, C, K, E, thiamine (B1), riboflavin (B2), niacin (B3), pyridoxine (B6), folic acid (B9), and pantothenic acid [16]. In general, apricot is especially rich in vitamins A and C [17]. Apricot contains organic acids, namely malic acid (500-900 mg/100 g] and citric acid (30-50 mg/100 g) as the main acids; it has also been reported to contain tartaric, succinic, oxalic, galacturonic, kinic, malonic, acetic, and fumaric acid [18]. These acids, which are natural components of many fruits and vegetables, reduce bacterial spoilage and provide flavor, taste, and shelf stability. They also play an important role in maintaining quality and determining nutritional value. Apricot kernels contain a considerable amount of protein and fat in 20-30% and 40-52%, respectively [19]. The average protein and fat ranges in apricot fruit are 1.4-2.0% and 0.4-0.6%, respectively. Despite the low amounts, apricot fruit also contains many essential amino acids [14].

Table 1: Proximate composition of apricot fruit [15].

Ingredients	Concentration (g/100 g fresh weight)
Water	83.00
Carbohydrates	11.00-13.00
Protein	1.40
Fat	0.40
Crude fiber	1.50-2.40
Ash	0.74

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Hakan Parlakpınar

A FORENSIC DETECTOR: NINHYDRIN

Hamdullah Kılıç

Ninhydrin (Fig. 1; also known as 2,2-dihydroxyindane-1,3-dione) reacts with primary and secondary amines to give a compound with a deep blue or purple color known as Ruhemann's purple. Thus, ninhydrin is a chemical indicator to test whether or not a compound has the terminal amine group. Ninhydrin is a white solid with a melting point of 250 °C and is soluble in polar solvents such as water, ethanol, and acetone at ambient temperature.

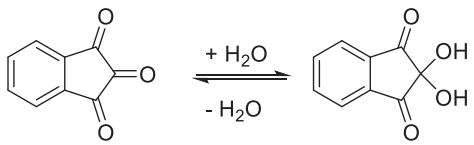


Figure 1. The structure of ninhydrin and its hydrates form.

How does ninhydrin help forensic science in obtaining evidence for theft detection? Fingerprints are composed of water, salts, lipids, vitamins, and amino acids. Commercially available visible stain theft detection kits contain ninhydrin, which is used to identify thieves by applying it to any object that may get stolen. When skin comes into contact with an object marked with ninhydrin,

the body's amino acids (Fig. 2) react with ninhydrin to create a very visible purple stain on the body lasting a few days.

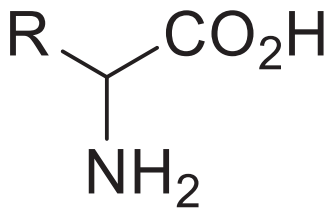
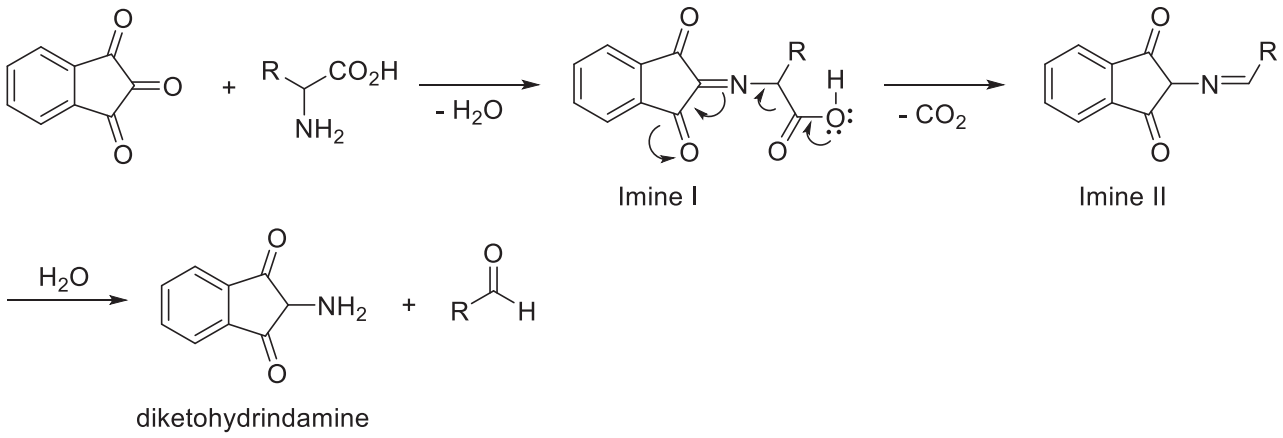
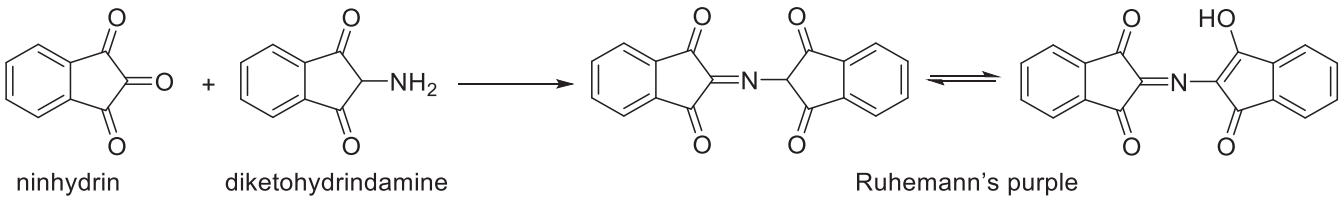


Figure 2. General structure of amino acids.

Now let us look at the chemistry behind ninhydrin. In the first step, ninhydrin is dehydrated and reacts with an amino group of the amino acid (except proline) to give an imine I. In the next step, decarboxylation from the imine I take place to give imine II. Then the imine II undergoes hydrolysis with water, forming an aldehyde and diketohydrindamine.



Finally, diketohydrindamine with primary amine moiety undergoes a condensation reaction with ninhydrin to give a colored product, which is called Ruhemann's purple.



WHAT ARE BEHIND CUBES?

Have you ever tried solving a Rubik's cube? I am sure you have and gave up working on it after completing only one face. Although you see Rubik's cube solution exhibitions on talent shows just as if the performers are magicians, there is, of course, an algorithmic way of explaining how they do it.

As a Rubik's cube solver from Turkey, I have been doing this as a hobby for 7 years. First of all, I saw one of my friends in middle school solving a Rubik's cube within 5 minutes after scrambling it. At that moment, my interest in Rubik's cubes was born, and so I did some quick research on the Internet and found out that there were a few methods to solve the cube. Because there are 43 quintillion combinations for a 3 × 3 × 3 Rubik's cube, I patiently watched videos to learn the "Beginner's Method" on YouTube. My first personal record without looking at the video was 5 minutes. I memorized only a few algorithms and did a lot of practice. Any progress? I improved my record to 1 minute. However, after that point, I realized that my record would not get better than that. Consequently, I decided to improve my technique of the most famous speedcubing method, known as the Friedrich Method. This method has plenty of algorithms to be memorized, yet instead of memorizing every single notation, coding those algorithms into your fingers rather than your mind consumes less time. Therefore, I developed a way of enhancing my memory, which assisted me in my academic and social life

since I was able to memorize everything much faster. Finally, my record was below 1 minute as I had expected.

I started following popular Rubik's cubers on social media, and so I found another division of speedcubing. Did you know that a Rubik's cuber takes care of his/her puzzles like a baby? I watched lots of unboxing and reviewing videos of different brands of Rubik's cubes to decide on my first professional cube and ordered one. 50 seconds! After that, I met the Turkish delegate of the World Cube Association (WCA), İskender Aznavur, and learned that many competitions were being held in one day all around the globe. Since I was fond of this hobby, I increased the number of puzzles in my collection by learning how to solve 2 × 2 × 2 and Pyraminx puzzles. Can you believe that there is a puzzle in the shape of a pyramid? Just wait for the next ones! I attended the national competition in Istanbul and met a lot of speedcubers. It was a stunning day for me since everybody around me was speaking the language of Rubik's cubes. Everyone was teaching and challenging each other. Although I competed in three categories, I witnessed all the categories. Blindfolded, one-handed, and Skewb categories were the most fascinating ones. In total, I took part in three different national competitions and in each of them I was so excited just like everyone else since sharing a common secret talent in an organization is superb.

Throughout all my experiences, I saw the impact of practicing a lot. My fingers got much stronger. Thus, I am now able to perform more than three moves per second, and I can use all of my fingers perfectly. In addition to that, when I tried learning blindfolded cube solving this process taught me a new aspect: 3-D thinking! Because I have to imagine all those next steps in my mind, I rotate the image of the Rubik's cube in my mind. Furthermore, this skill helped me even in science classes. It is very useful for me to imagine a 3-D model of a molecule in chemistry classes. As it was a hobby for me and had a lot of benefits, I was willing to widen my collection. Subsequently, I found the most extreme puzzles on the market such as the 7 × 7 × 7, gear cube, void cube, and 360 puzzles. By the way, some of these puzzles don't have a method. Therefore, I developed my own strategies and challenged myself. Also, one of the most important things that improve your solutions is foreseeing the next move. I wholeheartedly believe that when figuring out your next move becomes your way of thinking, it makes everything easier in your real life as well.

I was aware of the fact that there were not many Turkish online resources and so I created a YouTube channel called "*MyCubes And*I", in which I shared tutorials about how to solve Rubik's cubes and get prepared for competitions. Then I decided to share videos of me solving puzzles in the other countries I visit. Those moments are so special to me because many people gather around me while I am solving the puzzle in front of a tourist attraction, scramble the puzzles, and applaud me as I complete them. I even met an old Rubik's cuber in Barcelona and shot a video with him. Seeing how people get interested in such an extreme hobby satisfies me a lot.

To conclude, Rubik's cubes entered my life 7 years ago. However, my interest has never waned since then. It taught me a lot of things and enhanced my performance in real life in many aspects. This entertainment may be the most beneficial and interesting one in the world since you catch everybody's eyes once you start doing it. So, if I were you I would take the closest Rubik's cube, it is the best-selling toy of all time and so I am sure there is one close to you, and learn how to solve it!

Burak Alanyalioglu

Cultural Heritages

DIVRIGI GREAT MOSQUE AND HOSPITAL

Hüseyin YURTTAŞ

Esra HALICI

Burak Muhammet GÖKLER

Muhammed Emin DOĞAN

Located in the Divriği district of Sivas Province, the mosque was founded by the Mengüjek bey Ahmed Shah between 1228 and 1243; the hospital, on the other hand, was founded by Ahmed Shah's wife Turan Melek between the same dates and designed by architect Hürrem Shah, son of Ahlatlı Muğis.

The design of the mosque involves a sanctuary section consisting of five naves and it is covered with 23 different vaults and two domes. The front of the mihrab is covered with a star-shaped cone on the outside and dominates the mosque from the outside. The mosque has three entrances with the qibla portal (north crown portal), the bazaar portal in the west, and the shah portal in the east.

The stone decoration created by the craftsmen from Ahlat was reflected differently on all three portals. These ornamentations

Divriği, Mosque - Decoration

Divriği, Turkey - located in Central Anatolia, Divriği is a popular tourist destination. Here in particular the Great Mosque, a UNESCO World Heritage site

are regarded as unprecedented and unique examples in Anatolia, both in size and magnificence. The distinctive feature of Divriği Great Mosque and Hospital is that many motifs seem symmetrical but are actually asymmetrical and do not repeat each other. In addition, the double-headed eagle, which is considered to be the coat of arms of Alaaddin Keykubad, and the figures of Ahmed Shah's coat of arms, were carved into the western crown portal.

Built on the south wall of the mosque, the hospital consists of three iwans, the central part of which is covered with a skylight dome. A tomb is located in the northeast corner of the hospital. The crown portal of the building is monumental like the northern crown gate of the mosque but has a different design. Both male and female heads are embossed on both sides of the entrance door.

Divriği Great Mosque and Hospital was added to the UNESCO World Heritage List in 1985.

Divriği Mosque- Decoration

TODAY'S PROBLEM AND YESTERDAY'S ANSWER

Problem 5.

Alaaddin is trapped in a dark cave. In order to escape he should activate his enchanted lamp. He knows that if one simultaneously puts two magic sticks into the enchanted lamp then it will be activated and the gates of the cave will immediately open. There are 200 indistinguishable sticks and exactly 100 of them are magic. In each trial Alaaddin puts two sticks into the enchanted lamp. Determine the smallest possible value of n if Alaaddin can guarantee to activate the enchanted lamp in at most n trials.

Azer Kerimov

Answer of yesterday's problem :

There are at most 8 paintings in the exhibition.

Let us denote the colors by 1, 2,...,8. The collection of paintings colored by colors (1,2,3), (1,4,5), (1,6,7), (2,6,8), (3,4,8), (5,7,8), (3,5,6), (2,4,7) is an example for 8 paintings.

Now let us show that the number of paintings is at most 8. Let us fix a color c. Each of the remaining 7 colors can be used with c only in one painting. Therefore, the color c is used in at most 3 paintings and the total number of used colors is at most $8 \cdot 3 = 24$. Therefore, there are at most 8 paintings in the exhibition.

CHINA

Theoretical knowledge exam of the Chinese Chemistry Olympiad

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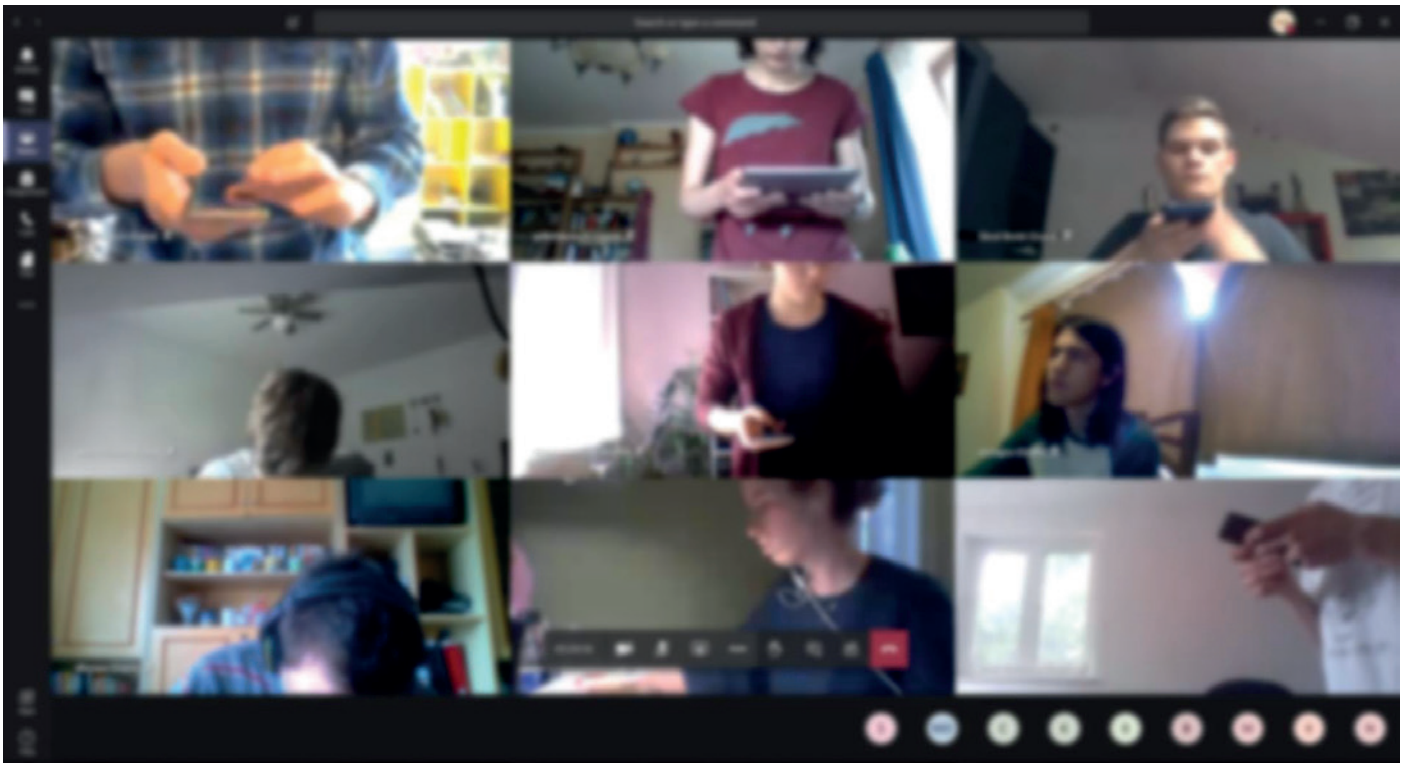

HUNGARY

MS Teams exam all over Hungary

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