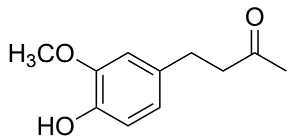
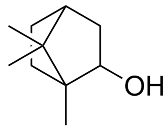
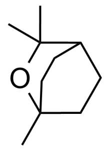
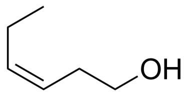
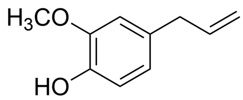
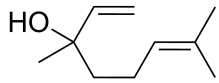
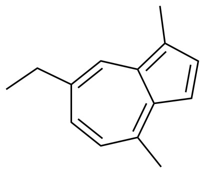
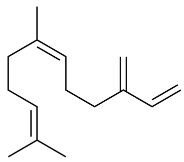
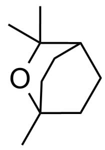
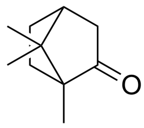
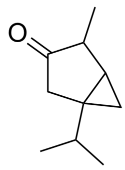
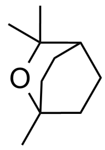
# T1. A journey through time: The secrets of Avicenna

| 7% | | | | | | |
|---|---|---|---|---|---|---|
| 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | ∑ |
| 3 | 4 | 3 | 4 | 7 | 4 | 25 |


A chemist found herself in the 11 th Century, where she met the renowned physician Avicenna. In Avicenna's laboratory, she discovered a blue elixir and a yellow mysterious stone. She brought them back to 2026. Determined to uncover their composition, she began her research.

## Part 1. The blue elixir

At first, the chemist compiled a table listing the names of the only four plants which she saw in Avicenna's lab that could have been used to prepare the elixir, and the compounds that can be extracted from these plants.

| Plants | Compounds that can be extracted | | |
|---|---|---|---|
| ***Zingiber*** |  |  |  |
| | **1** ($C_{11}H_{14}O_3$) | **2** ($C_{10}H_{18}O$) | **3** ($C_{10}H_{18}O$) |
| ***Hypericum*** |  |  |  |
| | **4** ($C_6H_{12}O$) | **5** ($C_{10}H_{12}O_2$) | **6** ($C_{10}H_{18}O$) |
| ***Chamomilla*** |  |  |  |
| | **7** ($C_{14}H_{16}$) | **8** ($C_{15}H_{24}$) | **3** ($C_{10}H_{18}O$) |
| ***Artemisia*** |  |  |  |
| | **9** ($C_{10}H_{16}O$) | **10** ($C_{10}H_{18}O$) | **3** ($C_{10}H_{18}O$) |

Using chromatography, she determined that the elixir consists of four different substances (**X**, **Y**, **Z** and **W**).

The chemist then discovered that **X** can isomerise into **Y** in an acidic medium and that **Y** has a plane of symmetry.

**1.1** **Identify X and Y.** 3.0 pt

**SOLUTION:**

**X:** 2 pt

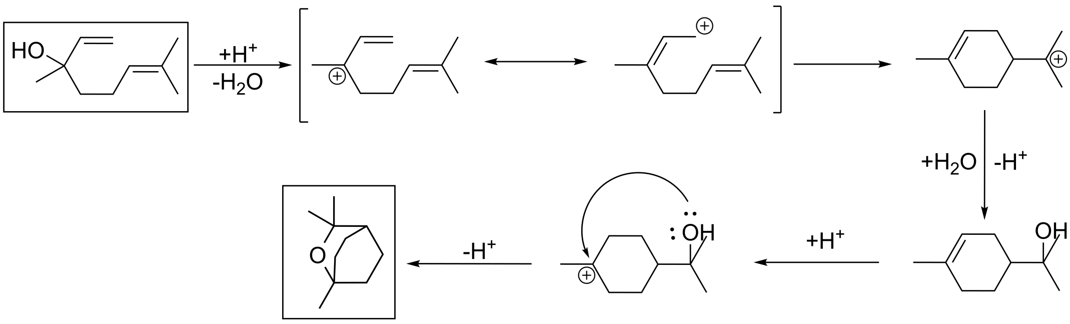
| | | | | |
|---|---|---|---|---|
| ☐ **1** | ☐ **2** | ☐ **3** | ☐ **4** | ☐ **5** |
| ✓ **6** | ☐ **7** | ☐ **8** | ☐ **9** | ☐ **10** |

**Y:** 1pt

| | | | | |
|---|---|---|---|---|
| ☐ **1** | ☐ **2** | ✓ **3** | ☐ **4** | ☐ **5** |
| ☐ **6** | ☐ **7** | ☐ **8** | ☐ **9** | ☐ **10** |

1 pt will be given if student switched **X** and **Y**.

Linalool **(6)** isomerises to cineole **(3)** in acidic solution as follows:

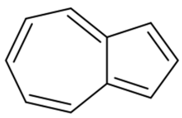


Chromatography also revealed it was substance **Z** that gave the elixir its blue colour. **Z** is a derivative of the well-known substance **A**, which has two perpendicular planes of symmetry. When heated, **A** isomerises into aromatic compound **B**, which has three mutually perpendicular planes of symmetry. When substance **Z** is chlorinated, a pair of peaks with an intensity ratio of 3:1 is observed in the mass spectrum at m/z 218 and 220, respectively.

**1.2** **Identify Z** and **draw** the structures of substances **A** and **B**. 4.0 pt

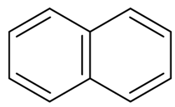
**SOLUTION:**

Chlorination of compound **Z** yields a monochlorinated product whose mass spectrum shows peaks at *m/z* 218 and 220 in a 3:1 ratio, characteristic of a molecule containing one chlorine atom (reflecting the natural abundance of $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$). Therefore, the molecular ion (M) of the $^{35}\mathrm{Cl}$ monochlorinated product is 218, indicating that the non-chlorinated precursor **Z** has a molecular mass of 184 (218 – 35 + 1 = 184). Compound **A** is azulene, a hydrocarbon distinguished by its deep blue colour – an uncommon property among organic molecules. Compound **Z** ($M = 184\ g$ mol$^{-1}$) is identified as chamazulene. Upon heating, azulene (**A**) isomerises into naphthalene (**B**), a thermodynamically more stable isomer.



azulene

**A**



naphthalene

**B**

**Z**: 1 pt

| | | | | |
|---|---|---|---|---|
| ☐ **1** | ☐ **2** | ☐ **3** | ☐ **4** | ☐ **5** |
| ☐ **6** | ✓ **7** | ☐ **8** | ☐ **9** | ☐ **10** |

1 pt for **A**
2 pt for **B**

The chemist extracted **W** from the elixir. When **W** was added to an aqueous $Fe^{3+}$ solution, a characteristic colour change was observed. Mass spectrometric analysis of **W** revealed the intensity ratio of $[M]^+ : [M+1]^+ = 9:1$, where $\mathrm{M}$ is the molecular ion. Assume carbon consists exclusively of $^{12}C$ and $^{13}C$, the natural isotopic abundance of $^{12}C$ is 98.9%, and all other elements are monoisotopic.

| | | |
|---|---|---|
| **1.3** | **Determine** the number of carbon atoms ($n$) from the mass spec data and **identify** **W**. **Show** your calculations. | 3.0 pt |

**SOLUTION:**
Since **W** gives a colour upon reaction with $Fe^{3+}$, it contains a phenol group. Two possible candidates with phenol group are eugenol ($C_{10}H_{12}O_2$) and zingerone ($C_{11}H_{14}O_3$). From mass spec data:

$$\frac{0.989^n}{0.989^{n-1} \times 0.011n} = 9 \qquad (1)$$

($n$ is the number of C atoms in **W**)

$$n = \frac{0.989}{0.011 \times 9} = 10$$

meaning that compound **W** has 10 carbon atoms. Thus, **W** is eugenol.

| | | | | |
|---|---|---|---|---|
| ☐ **1** | ☐ **2** | ☐ **3** | ☐ **4** | ✓ **5** |
| ☐ **6** | ☐ **7** | ☐ **8** | ☐ **9** | ☐ **10** |

1 pt for Equation 1
(other logically true equations to find carbons atoms will be also considered as true)
1 pt for carbon atoms ($n$)
**W:** 1 pt
If student struggled to find number of carbon atoms and choose one of the two options (zingerone or eugenol), 1 pt will be given

## Part 2. The mysterious stone

Avicenna had told her the **stone** was a stoichiometric compound. She dissolved it in dilute nitric acid. After that, she adjusted the pH of the solution to ~4 and added NaF. This led to the formation of precipitate **C** $\cdot\, x H_2O$, which contained 39.16% water by mass. Anhydrous **C** reacts with an excess of NaF to yield compound **D**, which contains 32.85% sodium and 12.85% of metal **Q** by mass, and is used in the industrial production of **Q**.

$$\textbf{Stone} \xrightarrow{HNO_3} \ldots \longrightarrow (pH \approx 4) \xrightarrow{NaF} \mathbf{C}\cdot \mathbf{x}H_2O\downarrow$$

$$\mathbf{C} \xrightarrow{NaF} \mathbf{D}$$

**1.4** **Identify** metal **Q** and compounds **C** $\cdot\, x H_2O$ and **D**. 4.0 pt

**SOLUTION:**

When NaF is added to the solution, precipitate **C** forms, which dissolves in an excess of NaF. This behaviour suggests the formation of a fluoride complex. Since **D** is used in the production of a metal, and only a few metals are obtained from fluoride complexes, the most probable candidates is aluminum. Considering, the ratio of Na:**Q** in **D** is $a : 1$

$$M(\mathbf{Q}) = \frac{23a}{0.3285} \times 0.1285 = 9a \qquad (2)$$

Option a = 3, where **Q** is aluminum, perfectly fits the conditions.
**C** $\cdot\, x H_2O$ is most probably hydrate of aluminum fluoride. To find number of water molecules($x$), we can use mass fraction of water, $0.3916 = \frac{(1.008\times2+16)\times x}{(1.008\times2+16)\times x+26.98+19\times3}$, $x = 3$
Thus, **C** $\cdot\, x H_2O$ is $AlF_3.3H_2O$.
$M(\mathbf{D}) = \frac{27}{0.1285} = 210\ g$ $mol^{-1}$
Thus, **D** is $Na_3AlF_6$.

**Q –** Al  **C** $\cdot\, x H_2O$ **–** $AlF_3 \cdot 3H_2O$  **D –** $Na_3AlF_6$

1 pt for Equation 2. 1 pt for each correct of **Q, C,** and **D**.

Avicenna told her that he found the **stone** in a coal deposit. The **stone** contains the anion of a highly symmetrical acid **F**. Reaction of **F** with $P_2O_5$ gives binary compound **G**, which contains 49.98% of oxygen by mass and has a three-fold symmetry axis. **F** can be prepared by oxidising compound **E** with potassium permanganate in an acidic solution. **E** contains 11.18% of hydrogen by mass and has a six-fold symmetry axis.

$$\mathbf{E} \xrightarrow[HNO_3]{KMnO_4} \mathbf{F} \xrightarrow{P_2O_5} \mathbf{G}$$

**1.5** **Draw** the structures of **E**, **F**, and **G**. 7.0 pt

**SOLUTION:**

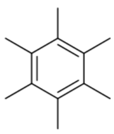
The highly symmetrical nature of the unknown compounds suggests that these are carboxylic derivatives of benzene, which form anhydrides when treated with phosphorus pentoxide. Thus, for **G**:

$$\mathrm{C{:}O} = \frac{50.02}{12.01} : \frac{49.98}{16} = \frac{1.333}{1}$$

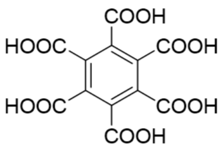
The corresponding minimum integer ratio is 4:3 ($C_4O_3$). Considering that **F** is a carboxylic acid and **G** is its anhydride, the presence of symmetry, and the aromatic nature of these compounds, one can propose that: **G** is $C_{12}O_9$, mellitic acid anhydride. **F** is $C_6(COOH)_6$, mellitic acid. Treatment of **E** with potassium permanganate leads to **F** (mellitic acid), indicating that **E** is a hexasubstituted benzene.

$$0.1118 = \frac{1.008x}{1.008x + 12.01y} \tag{3}$$

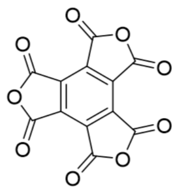
Solving this equation gives, x:y=9:6 Thus, the empirical formula of **E** is $C_6H_9$. The number of H atoms must be even, so, $C_{12}H_{18}$ or ($C_6(CH_3)_6$) ideally fits the conditions. Thus, **E** is ($C_6(CH_3)_6$).



**E**




**F**




**G**

0.5 pt for finding C:O ratio in **G**
2 pt for structure of **G**
2 pt for structure of **F**
0.5 pt for Equation 3
0.5 pt for empirical formula of **E**
1.5 pt for structure of **E**
(full marks will be given if student did not show calculations but did find all structures correctly)

Then, she analysed the **stone** thermogravimetrically in open air. A 10.00 g sample began to lose mass at approximately 100 °C and stopped at 5.75 g at 200 °C. A second drop in mass was observed at 400 °C, with a final mass of 1.50 g of compound **H** remaining constant at higher temperatures.

**1.6** **Determine** the chemical formulae of the **stone** and compound **H** using thermogravimetric data. 4.0 pt

**SOLUTION:**

Thermogravimetric data indicate that the mineral is a hydrate, as it starts to lose mass at about 100 °C. Thus, the molecular formula of the stone would be $Al_2(C_6(COO)_6) \cdot nH_2O$. Thus,

$$\frac{4.25}{(1.008 \times 2 + 16)n} = \frac{5.75}{26.98 \times 2 + 12.01 \times 12 + 16 \times 12} \tag{4}$$

n = 16

The final decomposition product is most likely aluminum oxide. To confirm this:

$$\frac{1.50}{M} = \frac{5.75}{26.98 \times 2 + 12.01 \times 12 + 16 \times 12} \tag{5}$$

$M$ = 101.8 $g$ mol$^{-1}$, which is very close to the molar mass of $Al_2O_3$.

Thus, **H** - $Al_2O_3$

**Stone:** $Al_2(C_6(COO)_6) \cdot 16H_2O$ (Honeystone)

1 pt for Equation 4

1 pt for Equation 5

1 pt for the formula of the **stone**

1 pt for the formula of the compound **H**
(full marks will be given if student found both formulae correctly without showing any equations).
If student has incorrect **Q** and/or incorrect **F** then credit can be given only if they propose an alternative answer that is **consistent with the data and chemically sensible.**