Summary: Synthesis of Salicylaldehyde and its Applications

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Introduction

Salicylaldehyde (SA) (C_6H_4CHO-2-OH) is a useful aromatic organic chemical. It is a common reactant for many synthesis, such as cyclic organic compounds like coumarin and organic ligand such as salan ligand. Salicylaldehyde is also crucial to our daily lives. In A. Ravin's medical publication, it is mentioned that SA can be used for detection of ketonuria in medical treatment. It also serves as a chelating agent with heavy metal ions such as Copper(II) ion, which is applicable to colorimetric analysis of the concentration of heavy metal ions in water sample. SA is also a precursor in total synthesis of coumarin ($C_9H_6O_2$), which is a white organic crystal with antibacterial activities.

However, salicylaldehyde is not commonly stored in secondary schools' laboratories. People can only buy a relatively large amount of salicylaldehyde with high price from chemical suppliers.

In our research project, we used a simple one-pot reaction to synthesize salicylaldehyde from phenol (C_6H_5OH), sodium hydroxide (NaOH) and chloroform ($CHCl_3$) which are available in school laboratory. The *synthesis*, *separation* and *identification* are carried under a normal secondary school laboratory without using advanced laboratory devices and apparatus.

Meanwhile, several *applications* of salicylaldehyde were also investigated, for instance the synthesis of coumarin, metal complex chelation and the medical detection of ketonuria.

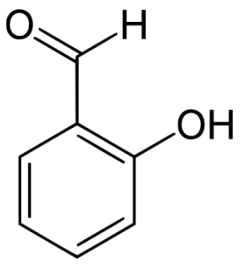


Figure 1: Chemical structure of salicylaldehyde

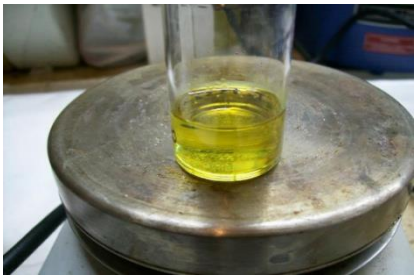
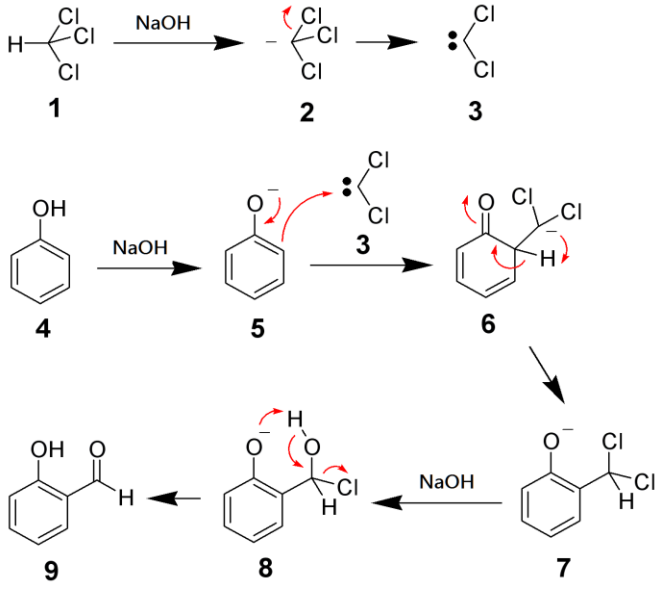


Figure 2: Appearance of salicylaldehyde

Part 1: Synthesis



By Reimer-Tiemann Reaction, phenol reacts with chloroform to form SA under refluxing for 1 hour in 65℃ water bath. This method is simple to carry out with a relatively high yield of SA obtained (~30%).

Figure 3: Reaction mechanism of converting phenol into salicylaldehyde by Reimer-Tiemann reaction.

Part 2: Separation

Steam distillation was used to obtain salicylaldehyde from the reaction mixture of part 1. Two techniques to extract the SA from distillate containing an oil layer and a liquid layer were found to be feasible, namely liquid-liquid extraction using chloroform and using dropper to draw the organic layer. Their yields were measured and compared at the end.

	1st trial	2nd trial	3rd trial
Mass of phenol reactant	3.76g	3.76g	3.76g
Mass of salicylaldehyde product	1.5084g	1.8932g	1.401g
Yield for salicylaldehyde	30.26%	37.98%	28.10%

Table: Mass of phenol reactant, salicylaldehyde and the yield in 3 trials

Part 3: Identification

In part 3, different chemical tests were carried out to try to identify the extracted components of distillate and the residue from part 2. Chemicals such as iron(III) chloride ($FeCl_3$) solution, 2,4-dinitrophenylhydrazine solution ($C_6H_6N_4O_4$) and concentrated sulphuric acid (H_2SO_4) were added to the samples of the extracted salicylaldehyde and aqueous layer, their colour changes were observed and compared in order to identify their chemical components. Below are the observation and the implications.

		Adding 2,4-DNPH (aq)	Adding conc. H_2SO_4 (l)
Steam distillation Aqueous layer	Observation	Little amount of orange-coloured precipitate was formed.	Turned milky
	Implication	Presence of small amount of aldehyde	Absence of aromatic aldehyde
Steam distillation Organic layer	Observation	A dark orange-coloured precipitate was formed. An orange oil droplet remain undissolved at the bottom of the 2,4-DNPH solution	From colourless to red
	Implication	1. Presence of large amount of aldehyde, 2. Undissolved orange oil droplet should be aldehyde	Presence of aromatic aldehyde (i.e. SA)

Table 2:

1. 2,4-dinitrophenylhydrazine solution ($C_6H_6N_4O_4$) can be used to detect ketone or aldehyde qualitatively. A positive test is shown by an orange or red precipitate. It cannot directly detect the presence of SA.

2. Concentrated sulphuric acid (H_2SO_4) can directly detect SA, the aromatic aldehyde by forming red precipitates.

Figure 4: 4 samples of aqueous layer and organic layer of distillate in LHS and RHS. Samples of both layers were tested by, (starting from left) $FeCl_3$ with HCl, $FeCl_3$, 2,4-DNPH and conc. H_2SO_4 (right) respectively.

Significance of the project

First, the project demonstrates the feasibility of conducting synthesis of SA in SECONDARY SCHOOL LABORATORY, which can be utilised for education purpose. Students can acquire practical skills and the principle behind reflux, steam distillation and identification of organic compounds, which can complement the HKDSE curriculum.

Second, the report exhibits the significance of SA in sewage treatment and medical examinations. Not only can SA be used to synthesize medical coumarin, it can also be used in detecting heavy metal ions in sewage by its chelating properties. Moreover, SA is useful in diagnosis of **ketonuria (尿酮症)**, as it can show the concentration of acetone which is one of the common ketone bodies.

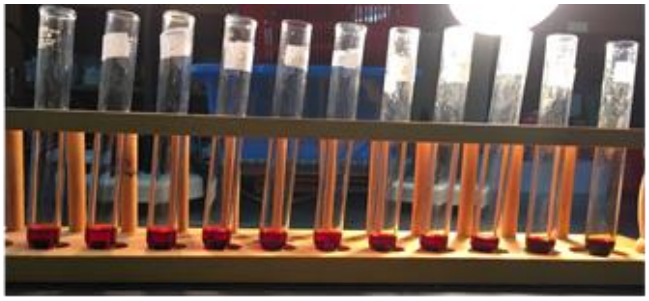


Figure 5: Increasing concentration of ketone from left to right showing increasing color intensity.

Figure 6: The resulting green solution (left) of copper(II) salicylaldehyde ($C_{14}H_{12}CuO_4$) complex and the original blue copper(II) sulphate ($CuSO_4$) solution.

Figure 7: Orange solid which contained coumarin obtained after Perkin reaction

Third, the report reveals several mistakes made by other reports and journals. According to Magpie's online report in www.sciencemadness.org, adding sodium hydrogensulphite into organic and aqueous layers can purify SA by forming sulfite adduct. However, no precipitation was observed in practice. It showed that this purification method was ineffective. Also, according to Kinza Aslam's jornal *"Synthesis and Application of Coumarin"*, iron (III) ion can be used to test for presence of SA. However, it can show colour change when it react with compounds with phenol group. It showed colour change when reacted with SA as SA contains phenol group. It is inaccurate to draw conclusion that iron (III) ion can indicate presence of SA. With new evidence in the report, corrections of the above reports are made. This shows that scientific knowledge is tentative, and subject to change when new evidence arises.