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Original article

Synthesis of Esters with Different Flavors using Fisher Esterification

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ABSTRACT

Among the most manufactured industrial organic chemicals are esters. They are widely used in a variety of household and commercial operations. This study was carried out using Fisher Esterification method to prepare the "Esters" from acids for the synthesis multiple flavors. The different flavors that have different physical properties were synthesized including: Scent of nail polish, spices, banana, pineapple flavor, oil, kiwi, purple flower, apple, pineapple, berries and grapes. Meanwhile, it was observed that when preparing ester flavors from liquid acids, they had a strong and clear smell compared to solid acids, which had a somewhat weak smell.

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INTRODUCTION

An ester is an organic molecule that is derived from a carboxylic acid and has an alkyl group in lieu of the hydroxyl group's hydrogen atom. The structure is the product of a carboxylic acid (the R-portion) and an alcohol (the R′-portion) [1]. Esters are extensively found in both nature and industry. In nature, fats are, in general, tri-esters derived from glycerol and fatty acids [1,2]. Esters are responsible for the aroma of many fruits, including apples, durians, pears, bananas, pineapples, and strawberries [3,4]. Every year, the industrial production of polyester yields several billion kilograms of polyester goods, among them cellulose acetate, acrylate esters, and polyethylene terephthalate [5]. Esters are widely used as food product preservatives [7] and flavoring ingredients [6], as well as significant perfume additions [8], in soap and cosmetic industry as fragrances [9] or in personal care product formulations [10].

Esterification is one of the most significant reactions in organic synthesis. Esters are ubiquitous in nature and in man-made chemical molecules [11]. The major examples of esterification products are biofuels such as biodiesel [12,13], solvents such as ethyl acetate and methyl acetate [14], paints and varnishes [15], pharmaceuticals [16], plastics and coatings [17] and some are used as herbicides and pesticides [6]. Esterification can happen in different ways: Esterification of carboxylic acids with epoxides, Alcoholysis of acyl chlorides and acid anhydrides, Alkylation of carboxylic acids and their salts, Esterification of carboxylic acids with alcohols The classic synthesis is the Fischer esterification, which involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent. This study was carried out using Fisher Esterification method to prepare the "Esters" from acids for the synthesis multiple flavors.

METHODS

The Fischer method was used to prepare the ester, which is a direct method using alcohol with acid in the presence of a strong mineral acid to accelerate the reaction [1] at private Sadeem laboratory.

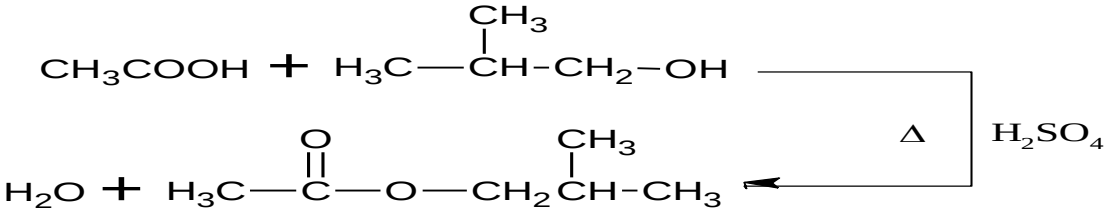
Materials

Formic acid, Acetic acid, Salicylic acid, Benzoic acid, concentrated sulfuric acid, 2-Propanol, Ethanol, Isobutanol, 5% Sodium bicarbonate anhydrous sodium sulfate and Methylene chloride.

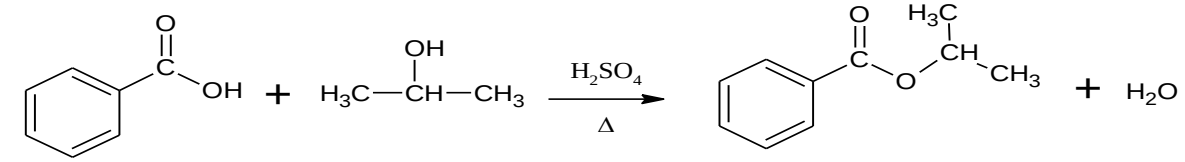
Experiment

Different sizes were used for solid carboxylic acids (6ml alcohol + 6ml H2O +1g carboxylic acid) and liquid carboxylic acids (9ml alcohol +3ml carboxylic acid). Then an appropriate amount of carboxylic acid was mixed and alcohol added to it in proportion to the amount of acid, then 3-4 drops of concentrated sulfuric acid were added, mixed and shacked in a circular manner (add the boiling chambers). Let the mixture boil while watching the reacted mixture in the beaker and record the temperature while continuing to heat for (40-60) minutes. Then, the mixture leaved at room temperature. the reaction mixture was transfer to a centrifuge tube, then 1 ml of methylene chloride added, shake the mixture, then slowly 3 ml of 5% sodium bicarbonate were added with mixing by spoon until the carbon dioxide be inactive. The upper layer is (the organic layer) and the lower layer is (the aqueous layer).

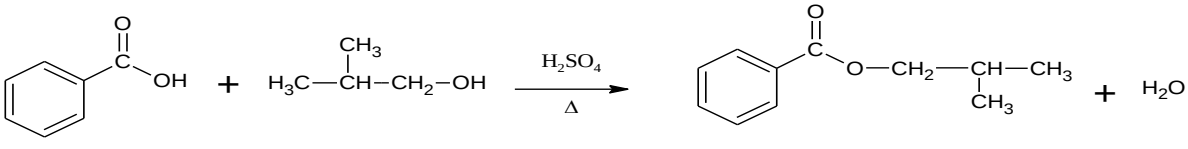
Explanatory equations for esters that were synthesized by fisher's method in the laboratory:



iso butyl acetate



iso propyl benzoate



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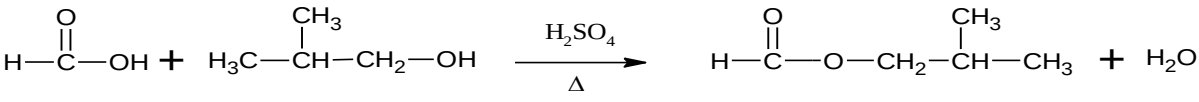
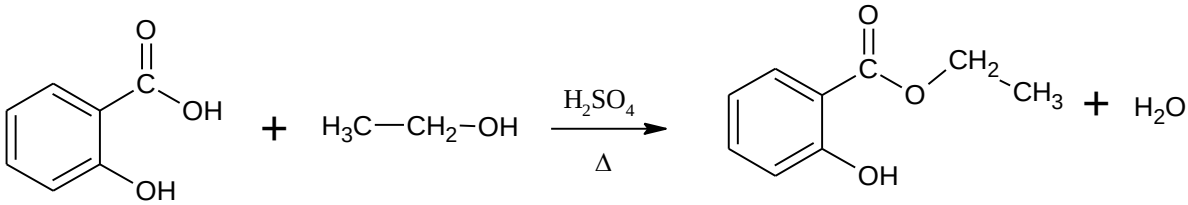
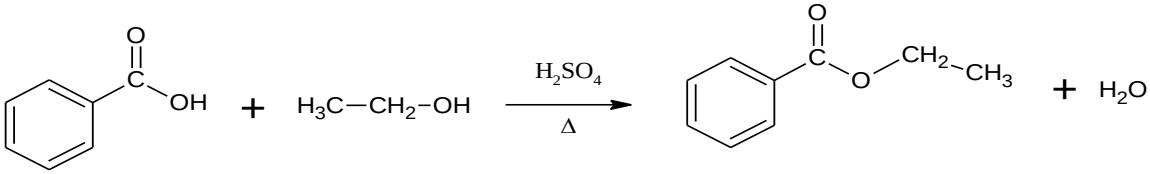


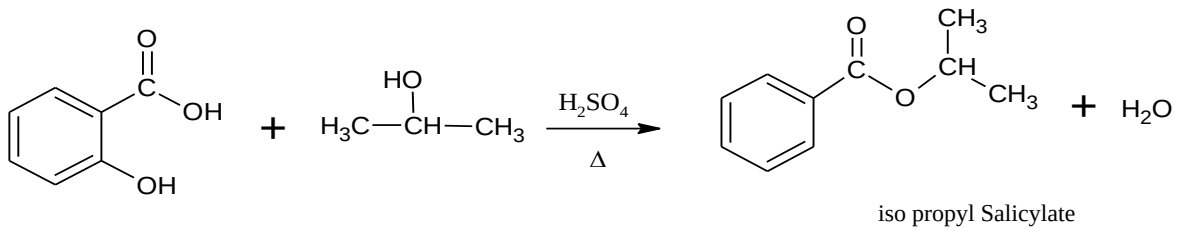
iso butyl formate



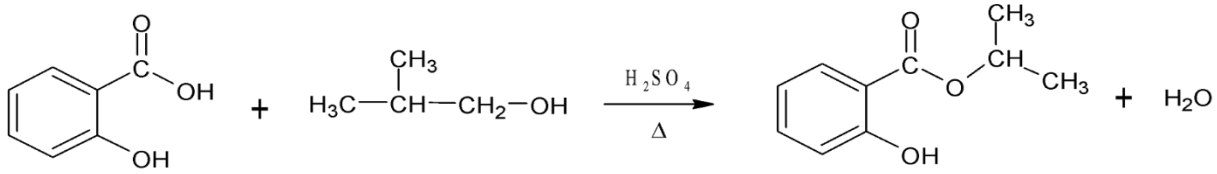
ethyl Salicylate



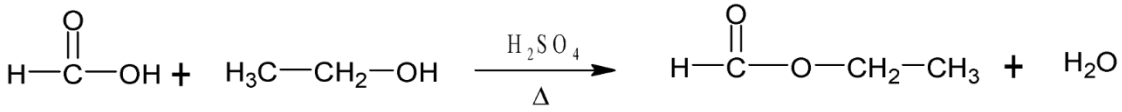
ethyl benzoate



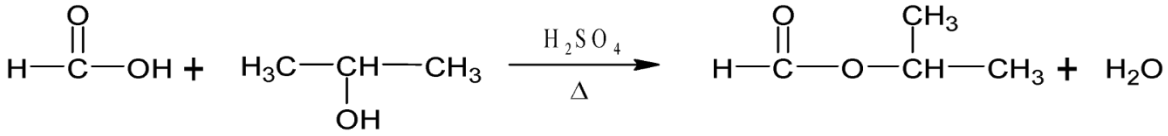
iso propyl Salicylate



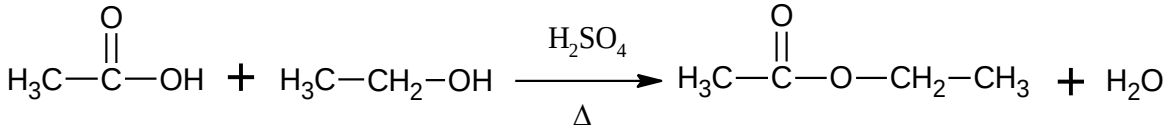
iso butyl Salicylate



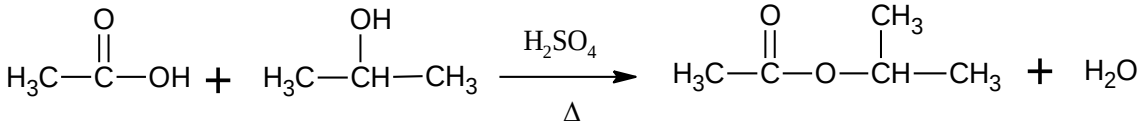
ethyl formate



iso propyl formate



ethyl acetate



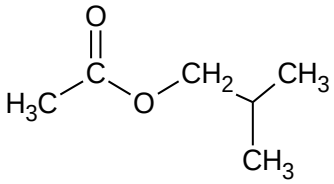
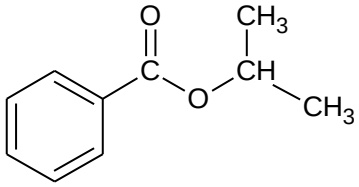
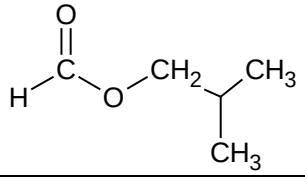
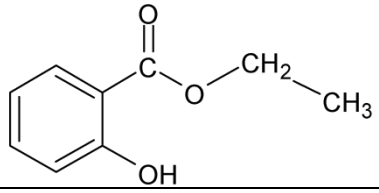
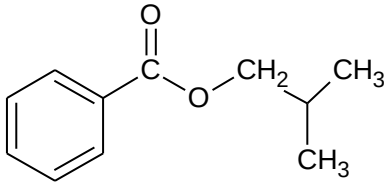
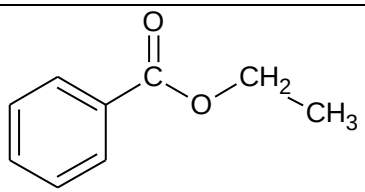
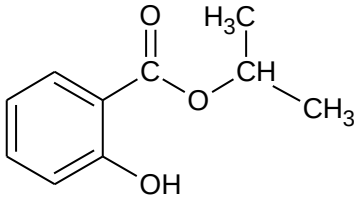
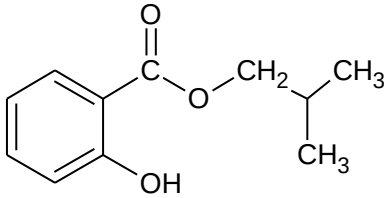
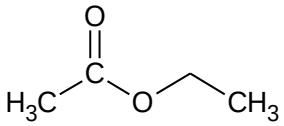
isopropyl acetate

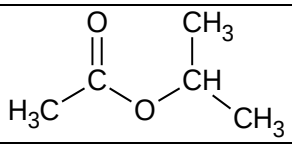
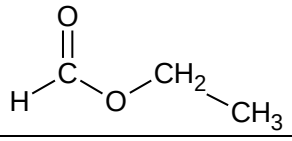
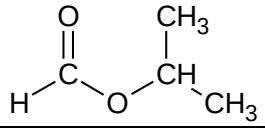
RESULTS AND DISCUSSION

This research was conducted in the Sadeem center laboratory, where iso butyl acetate was prepared from acetic acid and iso butyl alcohol and this produced smell of nail polish. Preparing iso propyl benzoate from benzoic acid and iso propanol alcohol, and from this reaction obtained the scent of mixed spices. Also, the iso butyl ester form was obtained from mixing formic acid with iso butyl alcohol to produced smell like bananas. Ethyl salicylate was prepared from salicylic acid with ethanol, and the smell of anise was obtained and it was very clear. Iso butyl benzoate was prepared from benzoic acid with iso butyl alcohol, and the oil smelled similar to the smell of olive pits. The ethyl benzoate ester was prepared from benzoic acid and ethanol, resulting in an odor resembling ripe kiwi.

In another reaction. the iso propyl salicylate ester was obtained from salicylic acid with iso propanol alcohol, without any odor observed. Meanwhile, iso butyl salicylate ester was yield from salicylic acid with iso butyl alcohol, and a floral scent resembling purple was observed. Ethyl acetate was prepared from acetic acid with ethanol and obtained the smell of pineapple smelled. The iso propyl acetate ester was prepared from acetic acid and iso propyl alcohol, and the was resulting smell similar to that of apples. The iso propyl form was prepared from formic acid and iso propyl alcohol and smelled like fermenting grapes. In Final reaction, the ethyl formate was yelied form of formic acid with ethanol, which resulted in a raspberry scent that was very clear (Table 1).

Table 1. The resulting esters and volumes

Ester	Molecular weight	Chemical structure	Product volume (ml)	Productivity (%)
Iso Butyl acetate	**$C_6H_{12}O_2$**		11.0	83.9
Iso propyl benzoate	**$C_{10}H_{12}O_2$**		11.8	79.2
Iso Butyl formate	**$C_5H_{10}O_2$**		6.7	82.1
Ethyl salicylate	**$C_9H_{10}O_3$**		1.0	52.1
Iso Butyl benzoate	**$C_{11}H_{14}O_2$**		2.8	63.6
Ethyl benzoate	**$C_9H_{10}O_2$**		3.9	69.6
Iso Propyl Salicylate	**$C_{10}H_{12}O_3$**		2.0	52.6
Iso butyl salicylate	**$C_{11}H_{14}O_3$**		1.0	50
Ethyl acetate	**$C_4H_8O_2$**		10.0	90.1

Iso propyl acetate	**C $_5$H$_{10}$O$_2$**		11.0	85.3
Ethyl formate	**C$_3$H$_6$O$_2$**		6.6	94.3
Iso propyl formate	**C$_4$H$_8$O$_2$**		7.0	83.3

Upon all above reactions, it was observed that when preparing ester flavors from liquid acids, they had a strong and clear smell compared to solid acids, which had a somewhat weak smell. In addition, when synthesizing esters in the laboratory using the Fisher method, it was noted that the resulting production rates of esters differed. The production percentages obtained from esters were as follows: ethyl formate, ethyl acetate, iso propyl acetate, iso butyl acetate, iso propyl format, iso butyl formate, iso propyl benzoate, ethyl benzoate, iso butyl benzoate, iso propyl salicylate, ethyl salicylate and iso butyl salicylate with following percentages: 94.3, 90.1, 85.3, 83.9, 83.3, 82.1, 79.2, 69.6, 63.6, 52.6, 52.1 and 50 respectively. It was noted that ethyl formate (94.3%) had the highest production percentage among the esters that were prepared, while iso butyl salicylate ester (50%) had the lowest productivity percentage. Last part of this work was illustrated explanatory equations for esters that were synthesized by fisher's method in the laboratory.

Table 2. Physical properties of the resulting esters

Ester	Molecular weight (g/ml)	Odor	Density (g/cm^3)	Color	Boiling point C^o	Melting point C^o
Iso butyl acetate	116.16	The smell of nail polish	0.871	Liquid Colorless	118	**- 99**
Iso Propyl benzoate	164.20	Smell of spices	1.011	Colorless oily liquid	216.0	**64.0**
Iso butyl formate	102.13	Banana smell	0.886	Liquid Colorless	97.92	**- 95.8**
Ethyl salicylate	166.17	Smell of anise	1.131	Yellowish liquid	232.5	**1.08**
Iso butyl benzoate	178.23	The smell of oil	0.999	Colorless oily liquid	242.0	**- 34.0**
Ethyl benzoate	150.17	Smell of ripe kiwi	1.050	Colorless oily liquid	212.0	**- 34.0**
Iso propyl salicylate	180.20	Odorless	1.031	Liquid Colorless	230.0	**1.0**
Iso Butyl Sali cylate	194.23	The scent of lilac flower	1.069	Liquid Colorless	261.0	**- 8.0**
Ethyl acetate	88.11	Smell of pineapple	0.9003	Liquid Colorless	77.1	**83.8**
Iso propyl acetate	102.13	The smell of apples	0.88	Liquid Colorless	89	**- 73**
Ethyl formate	74.079	Smell of berries	0.917	Liquid Colorless	129.2	**- 112**
Iso propyl format	88.11	The smell of fermenting grapes	0.883	Liquid Colorless	63.3	**- 80**

In a typical Fisher esterification process, a mixture of excess matching alcohols and carboxylic acids are heated in the presence of a catalyst. The reaction achieves equilibrium after a certain time governed by process kinetics and thermodynamics. To move the equilibrium in the direction of progress, it is necessary to supply an excess of one reactant (typically alcohol) or to remove water continuously [1, 18]. The yield of the product is ultimately compromised when

the reaction is unable to complete. Due to the onset of thermodynamic equilibrium, the reaction is constrained by a low overall conversion and a sluggish rate of reaction. Despite being commercially so important, the esterification process has yet to overcome these barriers in a cost effective and environmentally friendly way. A previous investigation utilizing a range of alcohols and acids under standard reflux settings revealed ester yields between 58–75% after 1-4 hours of reaction[19].

CONCLUSION

This work recommended to preparing esters from natural materials with different flavors and comparing them with chemically synthesized esters. As well as using natural sources, such as plants and flowers, will not introduces uncontrolled variables.

Acknowledgments

The authors thank the all departments that participated in this study.

Conflict of Interest

There are no financial, personal, or professional conflicts of interest to declare.

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تخليق الإسترات بنكهات مختلفة باستخدام استرة فيشر

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المستخلص

من بين المواد الكيميائية العضوية الصناعية الأكثر تصنيعاً هي الإسترات. يتم استخدامها على نطاق واسع في مجموعة متنوعة من العمليات المنزلية والتجارية. أجريت هذه الدراسة باستخدام طريقة فيشر إسترة لإعداد "الإسترات" من الأحماض لتوليف نكهات متعددة. تم تصنيع النكهات المختلفة التي لها خصائص فيزيائية مختلفة بما في ذلك: رائحة طلاء الأظافر والتوابل والموز ونكهة الأناناس والزيت والكيوي والزهرة الأرجوانية والتفاح والأناناس والتوت والعنب. وفي الوقت نفسه، لوحظ أنه عند تحضير نكهات الإستر من الأحماض السائلة، كانت لها رائحة قوية وواضحة مقارنة بالأحماض الصلبة، التي كانت لها رائحة ضعيفة إلى حد ما.

الكلمات المفتاحية. الأحماض الكربوكسيلية والكحوليات واسترة فيشر.