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Studying of Pechmann Condensation Products of Ethyl Acetoacetate with 2,7-Dihydroxynaphthalene

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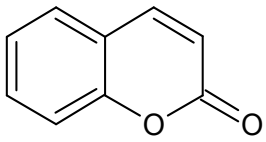
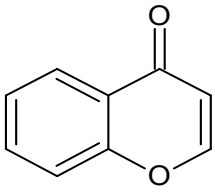
Abstract
Two benzocoumarins and a benzochromone were synthesized starting from 2,7-dihydroxynaphthalene and ethyl acetoacetate in the presence of Amberlyst-15 as condensing agent. The structures of the products have been elucidated by ^{1}H NMR, ^{13}C NMR, FT-IR spectral methods.
Keywords: 2,7-Dihydroxynaphthalene, Ethyl acetoacetate, Benzocoumarin, Benzochromon, Pechmann Condensation.

1. INTRODUCTION

Coumarins are a class of heterocyclic compounds containing oxygen as a member of the heterocyclic ring. The fusion of a pyrone ring with a benzene nucleus gives rise to a class of heterocyclic compounds known as benzopyrones, of which two distinct types are recognized: (1) benzo-α-pyrones, commonly called coumarins, and (2) benzo- γ -pyrones, called chromones, the latter differing from the former only in the position of the carbonyl group in the heterocyclic ring.[2,3]

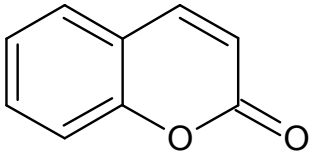


α-Benzopyrone



-Benzopyroneγ

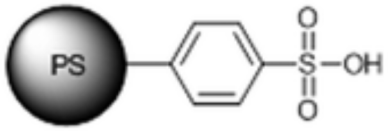
Coumarins (2H-1-benzopyran-2-ones) are important oxygen containing fused heterocycles used in drugs and dyes[1].Coumarins be bound their class name to 'coumarou' the vernacular name of the Tonka bean (Dipteryx odoratawilld, Fabaceae), from which coumarin itself was isolated in 1820[3,4].
The coumarins can be roughly categorized as the following[2,3,15] :
- Simple: these are the hydroxylated, alkoxylated and alkylated derivatives of the parent compound, coumarin, along with their glycosides.- Furanocoumarins: these compounds consist of a five membered furan ring attached to the coumarin nucleus, divided to linear and angular types with substituents at one or both of the remaining benzenoid positions.- Pyranocoumarins: members of this group are analogous to the furanocoumarins, but contain a six membered ring.- Coumarins substituted in the pyrone ring. Benzopyrone skeletal framework that have enjoyed isolation from plant[1-13] as well as total synthesis in the laboratory.



2H-1-benzopyran-2-one(Coumarin)

Coumarins occupy an important place in the realm of natural[1-13] and synthetic organic chemistry. They are used as anticoagulants,additives in food and cosmetics, and in the preparation of insecticides, optical brighteners, and dispersed fluorescent and laser dyes [14-21]. In addition, coumarins have been synthesised by several methods, including Pechmann [22], Perkin [23], Knoevenagel [24], Reformatsky [25], Wittig reactions [26,27], Baker et al [28], and Claisen-Rearrangement [29]. Among these, the Pechmann reaction is the most widely used method, as the reaction involves the use of simple starting materials, that is, phenols and β-ketoesters, in the presence of a variety of acidic condensing agents and gives good yields of 4- substituted coumarins. Several acid catalysts have been used in the Pechmann reaction including sulfuric acid, aluminum chloride , phosphorus pentoxide, trifluoroacetic acid, and others. However, these catalysts have to be used in excess; for instance, sulfuric acid in ten equivalents, trifluoroacetic acid in three to four equivalents, and phosphorus pentoxide is required in five equivalents. In all these methods, mixtures of the reagents were allowed to stand overnight or for a number of days, depending on their reactivity, or were heated above 150oC, and unwanted side products such as chromones were obtained. Recently, a number catalysts such as BiCl3, Sm(NO3)3_6H2O, InCl3, TiCl4, Yb(OTf)3, p-Toluenesulfonic acid, AgOTf, ceric ammonium nitrate, montmorillonite clay, silica sulfuric acid, chloroaluminate

ionic liquid, heteropolyacids ,Bi(NO3)3_5H2O, sulphamic acid, sulfonic acid nanoreactor, and FeCl3 under ultrasound irradiation [30-46] have been used in the Pechmann condensation. However, each of these methods has its own advantages but also suffers from one or more disadvantages, such as prolonged reaction times, low yields, use of harmful organic solvents, and requirement of excess of catalyst and reagents, and harsh reaction conditions. In continuation of our work to develop new synthetic methodologies, herein in this work we were directed toward treatment of 2,7-dihydroxynaphthalene with ethyl acetoacetate under solvent-free conditions in the presence of a catalytic amount of Amberlyst-15[47,48] as heterogeneous catalyst Figure (1) .



PS= PolyStyrene

Figure (1): General formula of Amberlyst-15

It is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group. Itserves as an excellent source of strong acid. It can also be used several times. Amberlyst 15, Hammett acidity approximately to one sulfonic acid group, Amberlyst-15 is of specific interest in this study since it has been reported to be a solid superacid catalyzing a variety of organic conversions and reactions such as esterification, transesterification, Michael addition, aza-Michael addition, Prins cyclization, Friedel-Crafts alkylation, acylation, metal free hydroarylation,hydroalkylation, halogenation, protection of carbonyls, amines, deprotection of acetals,acetates, Boc-protected amines, cleavage of epoxides, crossed-aldol condensation, synthesis of quinolines, pyrazolines, indolinones, acridines, xanthenes, coumarins, benzopyrans theaspirane, furans, and substituted phosphonates. Applications of this catalyst allow mild and highly selective transformations and synthesis in a facile and environmentally friendly manner[47,48].

The method has advantages in terms of yields, short reaction times, ease of operation, use of relatively nontoxic catalyst and and solvent free, decrease side products such as chromones

2. EXPERIMENTAL

2.1. Apparatus

spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, rotary evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck, thin layer chromatographic of preparatory glass coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

2.2- raw materials and reagnts

dihydroxynaphthalene, ethyl acetoacetate(sigma aldrich & merck), dimethylformamide, NaOH, Conc.HCl acid and some solvents (99% by Merck) ,amberlyst-15 (99% by sigma aldrech)

2.3.Experimental Procedure

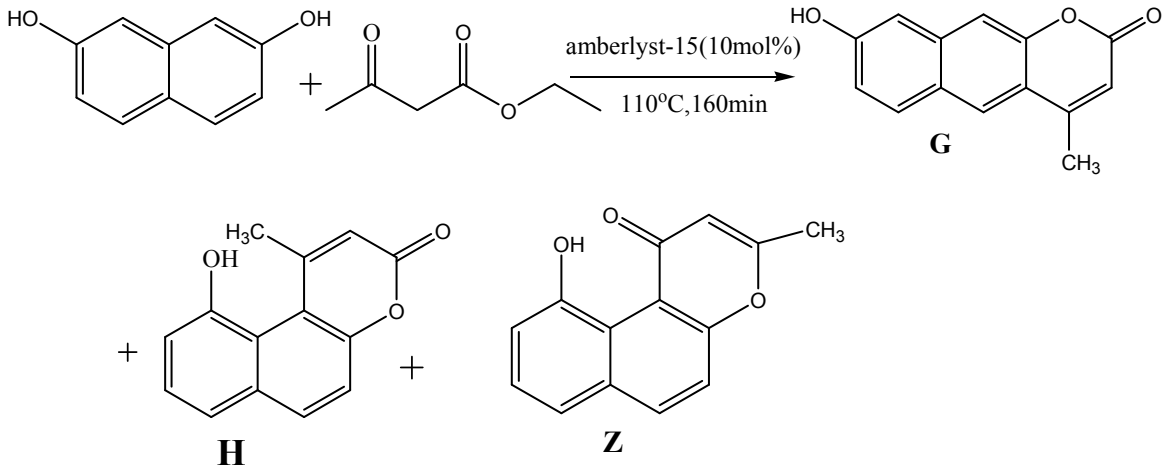
General procedure

8-Hydroxy-4-methyl-benzo[g]chromen-2-one (G), 9- Hydroxy-1-methyl-benzo[f]chromen-3-one (H), The chromone's compound: 9-Hydroxy-3-methyl benzo[f]chromen-1-one(Z)

A mixture of 2,7-dihydroxynaphthalene (0.8 g, 5mmol) in ethyl acetoacetate (1.6mL, 15 mmol) as a suspension was slowly added with (10 mol %) of Amberlyst-15 at 110 ºC by magnetically stirred for 160 min. After the addition of 100 mL ice/water, filtered, washed with water and dried on filter paper open air to give a crude mixture of products which were taken into ethyl alcohol and the insoluble material was filtered. Then the insoluble material was recrystallized from dimethylformamide to obtain Z (318 ºC decomp, yield: 5%.) as white powder. The solution was evaporated to dryness on a steam bath and the remaining solid product was dissolved in 10% aqueous NaOH. The insoluble material was filtered, acidified and recrystallized from ethyl alcohol to obtain G (m.p. 274 ºC, yield: 35%.)) as yellowish powder. Conc.HCl was added to the filtrate until pH between G and H. A solid was obtained from the filtrate after standing overnight. Then it was washed with water, dried and recrystallized from ethyl alcohol to give H (m.p. 284 ºC, yield:60%.)) as yellowish powder.. The physical data (mp, NMR, IR) of these known compounds were found to be identical with those reported in the literature.

RESULTS AND DISCUSSION

In the Pechmann reaction of 2,7-DHN with Amberlyst-15, we obtained an a linear and angula benzocoumarins and also we distinguished a very small amount of a new product and identified it as a benzochromone Scheme 1 under solvent-free condtions in the presence of a catalytic amount of Amberlyst-15 (10 mol%) at 110o C.



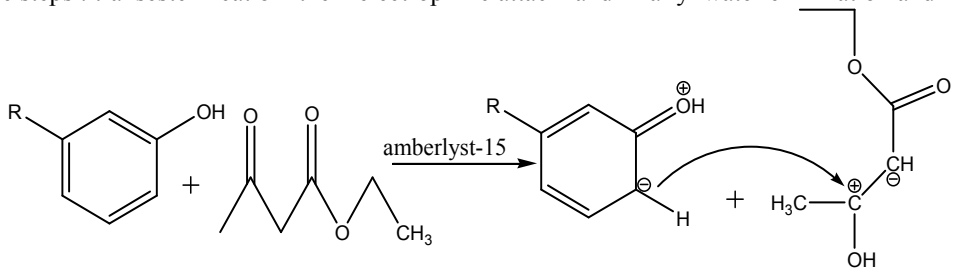
Scheme 1. Synthesis of 8-Hydroxy-4-methyl-benzo[g]chromen-2-one (G), 9- Hydroxy-1-methyl-benzo[f]chromen-3-one (H),and the chromone's compound: 9-Hydroxy-3-methyl benzo[f]chromen-1-one(Z) by using Amberlyst-15 as a catalyst.

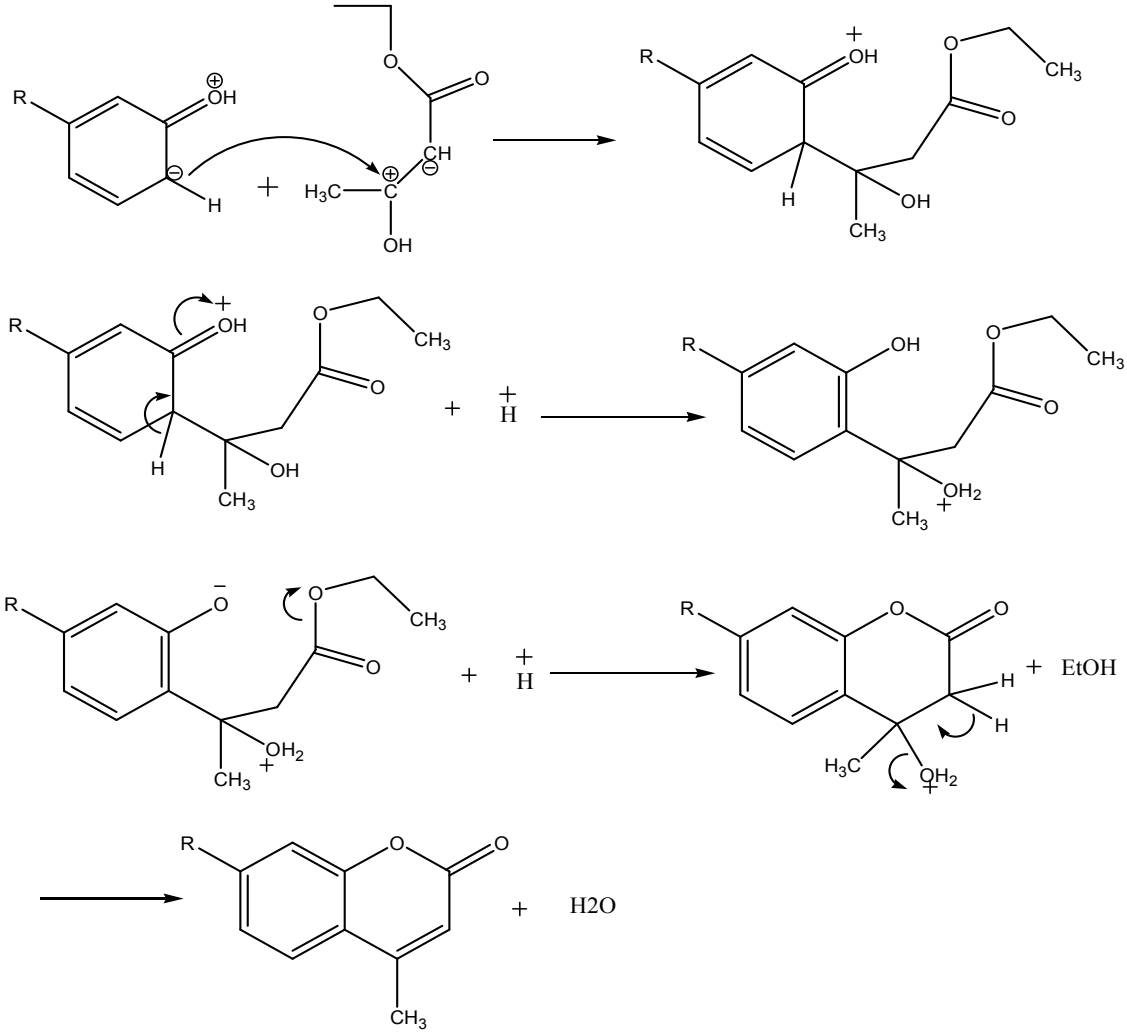
The previous studies researchers observed that Pechmann reaction yields two isomeric benzocoumarins with H2SO4 and many side products When we performed the same reaction with Amberlyst-15 , we distinguished a very small amount of only side product and identified it as a benzochromone.

For the differentiation of linear/angular benzocoumarin, application of the peri-proximity effect in 1H NMR and 13C NMR spectroscopy was envisaged as an appropriate technique. This effect causes a deshielding of the high intensity. The NMR examination of products in DMSO showed linear and angular benzocoumarins due to two methyl peaks observed at 2.49 δ and 2.84 δ indicating the nonperi-substitued methyl of (G) and the peri-substitued methyl of (H) respectively. The alkyl region of the 13 C NMR showed two methyl signals at 17.99 δ for linear isomer and 25.54 δ for angular isomer again characteristic of the aforementioned environments.

For the differentiation of benzocoumarin and benzochromone, IR spectroscopy were used. The carbonyl peak(C=O) of linear/angular benzocoumarin at about 1719 cm−1 and 1704 but the carbonyl peak of benzochromone at about 1639 cm−1 appeared in IR.

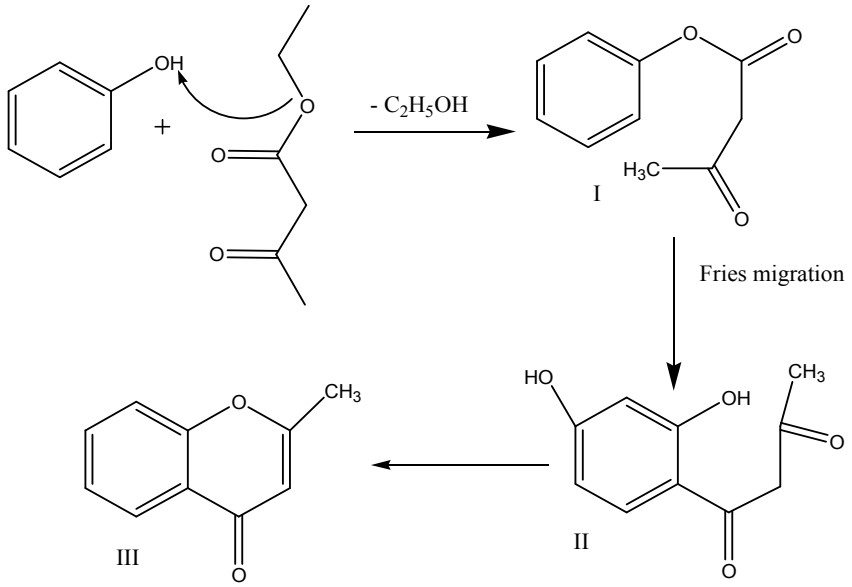
the formation of benzocoumarin can be explicated by mechanism of Pechmann–Duisberg (Scheme 2) wich include three steps : transesterification then electrophilic attack and finally water elimination and ring closure





Scheme 2. Plausible mechanism for the pechmann condensation of phenols and β–keto esters by Amberlyst-15

While formation of chromone side-product can be explicated by Ahmed and Desai mechanism wich include that the electrophilic attack as the first step, followed by Fries migration and finally water elimination and ring closure(Scheme 3)



Scheme 3 . Mechanism proposed by Ahmed and Desai. The lower route indicates the proposed side-reaction.

4. Conclusions

The procedure has been described for the synthesis of coumarin derivatives through the Pechmann reaction and an efficient one-pot synthesis using amberlyst-15 as a solid catalyst under solvent-free conditions. The advantages of this procedure are short reaction times, operational simplicit, and high yields. In many cases the product crystallized directly from the reaction mixture in high purity without using column chromatography. We believe that this method exhibits a practical alternative to existing procedures for the synthesis of these heterocyles.

5. Characterization of the products

8-Hydroxy-4-methyl-benzo[g]chromen-2-one (G):

1H NMR(DMSO-d6, 400MHz) δ 2.49(s, 3H, 4-CH3 overlapped by DMSO-d6), 6.32(s, 1H, 3-H), 7.10(dd, J=9Hz, J=2Hz, 1H, 7-H), 7.15(d, J=2Hz, 1H, 9-H), 7.59(s, 1H, 10-H), 7.93(d, J=9Hz, 1H, 6-H), 8.24(s, 1H, 5-H), 10.21(s, 1H, OH). 13C NMR(DMSO-d6, 400MHz) δ 17.99, 107.53, 109.85, 113.30, 116.74, 118.96, 124.45, 125.64, 130.63, 136.29, 150.18, 153.021, 157.48, 159.89. IR(KBr) IR(KBr) (v, cm-l):3340(O-H),1719(C=O), 2988 (Csp3-H), 3061(Csp2-H), 1200 (C-O), 1530+1655(C=Caromatic),1627(C=Calken).

9- Hydroxy-1-methyl-benzo[f]chromen-3-one (H):

1H NMR (DMSO-d6, 400MHz) δ 2.84 (s, 3H, 1-CH3), 6.40(s, 1H, 2-H), 7.13 (dd, J=9Hz, J=2Hz, 1H, 8-H), 7.26 (d, J=9Hz,1H, 5-H), 7.89 (d, J=9Hz, 1H, 7-H), 7.99 (d, J=2Hz, 1H, 10-H), 8.02 (d, J=9Hz, 1H, 6-H), 10.12 (s, 1H, OH). 13C NMR(DMSO-d6, 400MHz) δ 25.54, 108.23, 112.57, 113.69, 114.76, 116.86, 125.13, 131.14, 131.48, 133.62, 154.66, 154.82, 157.3, 159.25. IR(KBr) (v, cm-l):3451(O-H),1704(C=O), 2928 (Csp3-H), 3071(Csp2-H), 1250 (C-O),1500+1610(C=Caromatic),1637(C=Calken).

9-Hydroxy-3-methyl benzo[f]chromen-1-one(Z):

1H NMR(DMSO-d6, 400MHz) δ 2.40 (s, 3H, 2-CH3), 6.33 (s, 1H, 3-H), 7.15 (dd, J=8.75Hz, J=2.5Hz, 1H, 8-H), 7.39 (d, J=9Hz, 1H, 5-H), 7.89(d, J=9Hz, 1H, 7-H), 8.13(d, J=9Hz, 1H, 6-H), 9.32(d, J=2.5Hz, 1H, 10-H), 10.12(s, 1H, OH). 13C NMR(DMSO-d6, 400MHz) δ 19.18, 108.95, 112.50, 113.79, 114.64, 117.68, 124.43, 130.03, 132.03, 135.13, 157.75, 158.36, 163.63, 178.94. IR(KBr): IR(KBr) (v, cm-l):3465(O-H),1639(C=O), 2928 (Csp3-H), 3071(Csp2-H), 1131 (C-O),1510+1600(C=Caromatic),1624(C=Calken).

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