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INVESTIGATION 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 (2,7-DHN) and ethyl acetoacetate (EAA) in the presence of sulphuric acid solutions as condensing agent. The structures of the products have been elucidated by ^{1}H NMR, ^{13}C NMR, IR and Mass spectral methods. Increasing concentration of H_2SO_4 promotes the yield of benzochromone **3** is the most important observation.

Keywords: 2,7-Dihydroxynaphthalene, Ethyl acetoacetate, Benzocoumarin, Benzokromon, Pechmann Condensation.

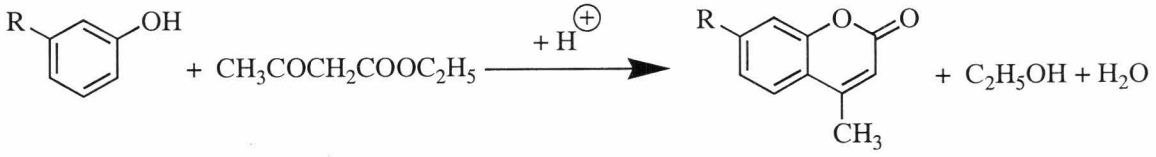
2,7-DİHİDROKSİNAFTALİN İLE ETİL ASETOASETATIN PECHMANN KONDENSAZYON ÜRÜNLERİNİN İNCELENMESİ

ÖZET: İki benzokumarin ve bir benzokromon, kondensazyon aracı olarak sülfürik asid çözeltisi varlığında 2,7-dihidroksinaftalin ve etil asetoasetat (EAA)' tan başlayarak sentezlendi. Bu bileşiklerin yapıları ^{1}H NMR, ^{13}C NMR, IR ve Kütle spektral metodlarla açıklandı. Artan H_2SO_4 konsantrasyonu en önemli gözlem olan benzokromonun **3** verimini arttırır.

Anahtar Kelimeler: 2,7-Dihidroksinaftalin, Etil asetoasetat, Benzokumarin, Benzokromon, Pechmann Kondensazyonu.

INTRODUCTION

Pechmann and Duisberg[1] found that phenols condense with β-ketonic esters in the presence of sulphuric acid, giving coumarin derivatives:



This reaction has found extensive applications in the synthesis of various coumarin derivatives substituted on the pyrone ring. In all instances in which sulphuric acid is the condensing agent except two, coumarins are obtained. As exceptions, 2-Naphthol[2] gives a mixture of a coumarin and a chromone, and 4-chloro-3,5-dimethylphenol[3] affords a chromone exclusively.

Pechmann condensation with 2,7-DHN and ethyl acetoacetate in presence of sulphuric acid solution has been studied by many researchers. Buu-Hoi and Lavit[4] obtained an angular benzocoumarin **2** (m.p. 277 °C) by using dry HCl as condensing agent. Pardanani and Sethna[5] have reported that they obtained a linear benzocoumarin **1** (m.p. 267 °C) with 80 % H_2SO_4. The same group obtained an angular benzocoumarin **2** (m.p. 276 °C) using dry HCl as catalyst and a benzochromone **3** (mp 285 °C) by refluxing in diphenyl ether. Wolfbeis[6] has reported an angular benzocoumarin **2** (m.p. 321-324 °C)

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using conc. H_2SO_4. Günaydın and Oyman[7] have used tetraethylmetaphosphate (PPE) and obtained both a linear benzocoumarin **1** (m.p. 219 °C) and an angular benzochromone **3** (m.p. 235 °C). Tao, Qian and Fan[8] observed both a linear and an angular benzocoumarins with 80 % H_2SO_4. And finally, We[9] have reported an angular benzocoumarin **2** (m.p. 282 °C) using PPA.

EXPERIMENTAL SECTION

General. Melting points were taken on a digital melting point apparatus electrothermal 9200. Infrared spectra were recorded on a Shimadzu IR spectrophotometer, mass spectra on a Zab spec. 70 eV, ^{1}H NMR and ^{13} C NMR on a Bruker-Spectrospin DPX avance 400 ultra shield using TMS as internal standard commercial reagents and solvents were purchased from standard chemical suppliers and without further purification.

8-hydroxy-4-methyl-2*H*-naphtho[2,3-b]pyran-2-one(1), 9-hydroxy-1-methyl-3*H*-naphtho[2,1-b] pyran-3-one (2) and 9-hydroxy-2-methyl-4*H*-naphtho[2,1-b]pyran-4-one (3). A mixture of 2,7-dihydroxynaphthalene (1.6 g, 10 mmol) in ethyl acetoacetate (3.9 mL, 31 mmol) as a suspension was slowly added to a 10 mL aqueous solutions of H_2SO_4 (different concentrations) at 0 °C by magnetically stirred. The mixture was kept for 24h at room temperature and 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 **3** (318 °C decomp.) 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 **1** (m.p. 274 °C) as yellowish powder. Conc.HCl was added to the filtrate until pH between 1 and 2. A solid was obtained from the filtrate after standing overnight. Then it was washed with water, dried and recrystallized from ethyl alcohol to give **2** (m.p. 284 °C) as yellowish powder.

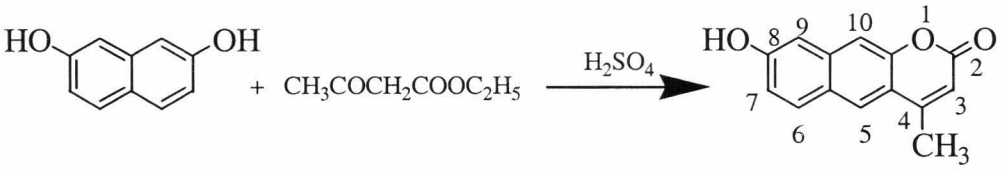
8-hydroxy-4-methyl-2*H*-naphtho[2,3-b]pyran-2-one (1): ^{1}H NMR(DMSO-d_6, 400MHz) δ 2.49(s, 3H, 4-CH_3 overlapped by DMSO-d_6), 6.32(s, 1H, 3-H), 7.10(dd, J=9Hz, J=2Hz, 1H, 7-H), 7.15(d, J=2Hz, 1H, 9-H), 7.59(s, 1H, 10-H), 7.93(d, J=9Hz, 1H, 6-H), 8.24(s, 1H, 5-H), 10.21(s, 1H, OH). ^{13}C NMR(DMSO-d_6, 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. MS(EI, 70eV) m/z : 226(M^+), 209, 198, 181, 169, 152, 141, 126, 115. IR(KBr) : 3360, 1705, 1680, 1622, 1564, 1478, 1446, 1398, 1331, 1238, 1139, 1062, 924, 892, 832, 819, 739, 566, 537, 512, 464 cm^{-1}.

9-hydroxy-1-methyl-3*H*-naphtho[2,1-b]pyran-3-one (2): ^{1}H NMR (DMSO-d_6, 400MHz) δ 2.84 (s, 3H, 1-CH_3), 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). ^{13}C NMR(DMSO-d_6, 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. MS(EI, 70eV) m/z : 226(M^+), 211, 209, 198, 181, 169, 155, 152, 141, 127, 115, 113. IR(KBr): 3312, 1686, 1622, 1555, 1536, 1440, 1408, 1376, 1356, 1228, 1139, 1062, 953, 832, 729, 662, 582, 537, 512, 483, 441 cm^{-1}.

9-hydroxy-2-methyl-4*H*-naphtho[2,1-b]pyran-4-one (3): ^{1}H NMR(DMSO-d_6, 400MHz) δ 2.40 (s, 3H, 2-CH_3), 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). ^{13}C NMR(DMSO-d_6, 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. MS(EI, 70eV) m/z : 226(M^+), 209, 198, 186, 181, 169, 158, 139, 130, 113. IR(KBr): 3440, 3120, 2928, 2720, 1641, 1612, 1571, 1536, 1472, 1449, 1372, 1350, 1318, 1260, 1222, 1200, 1145, 1062, 969, 899, 880, 838, 704, 620, 582, 550, 505, 457 cm^{-1}.

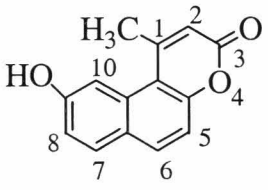
RESULTS AND DISCUSSION

In the Pechmann reaction of 2,7-DHN with H_2SO_4, we obtained an angular and a linear benzocoumarins and also an angular benzochromone.



1

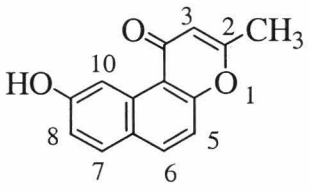
8-Hydroxy-4-methyl-2H-naphto[2,3-b]pyran-2-one



2

9-Hydroxy-1-methyl-3H-naphto[2,1-b]pyran-3-one

+



3

9-Hydroxy-2-methyl-4H-naphto[2,1-b]pyran-4-one

In previous studies researchers observed that Pechmann reaction yields two isomeric benzocoumarins with 80 % H_2SO_4. When we performed the same reaction, we distinguished a very small amount of a new product and identified it as a benzochromone.

When we compare IR and mass spectral data of the compound Wolfbeis claimed, we observed irrelevancies. 186 mass value on Mass spectrum and 1645 cm^{-1} absorption value on IR is characteristic of a benzochromone, not a benzocoumarin, so that the structure of Wolfbeis may be incorrect. We believe that the product is benzochromone **3** judging from our spectral data.

For the differentiation of linear/angular benzocoumarin, application of the peri-proximity effect in ^1H NMR and ^{13}C 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 **1** and the peri-substitued methyl of **2** 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 and mass spectroscopy were used. The carbonyl peak of benzocoumarin at about 1680 cm^{-1} and carbonyl peak of benzochromone at about 1640 cm^{-1} appeared in IR.

Methylacetylene peak (186) which characterises benzochromone was monitored in mass spectroscopy. This peak was not exist in the mass spectrum of benzocoumarin. The structure of our compounds has been proved based on these data.

Experimental results are given in Table 1.

Table 1. Results from reactions of 2,7 DHN and EAA by using at different concentration H_2SO_4 solutions:

Acid Percentage (%)[a]	Benzochromone (**3**) (%)	Lin. Benzocoumarin (**1**) (%)	Ang. Benzocoumarin (**2**) (%)
95	8.2	3.1	8.8
92	7.4	10.2	9.05
89	3.7	18.0	15.4
86	3.2	24.5	21.8
83	1.5	31.7	27.3
80	0.5	37.6	29.4

[a] (H_2SO_4 in H_2O)

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