

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

SYNTHESIS OF NEW CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES AND OF 2-AMINOQUINOLINE-3-CARBONITRILES

Saleh M. Al-Mousawi^a; Yehia M. Elkholy^a; Mohammad A. Mohammad^a; Mohammad H. Elnagdi^a

^a Department of Chemistry, Faculty of Science, University of Kuwait, KUWAIT

To cite this Article Al-Mousawi, Saleh M. , Elkholy, Yehia M. , Mohammad, Mohammad A. and Elnagdi, Mohammad H.(1999) 'SYNTHESIS OF NEW CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES AND OF 2-AMINOQUINOLINE-3-CARBONITRILES', *Organic Preparations and Procedures International*, 31: 3, 305 – 313

To link to this Article: DOI: 10.1080/00304949909458324

URL: <http://dx.doi.org/10.1080/00304949909458324>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**SYNTHESIS OF NEW CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES
AND OF 2-AMINOQUINOLINE-3-CARBONITRILES**

Saleh M. Al-Mousawi, Yehia M. Elkholy, Mohammad A. Mohammad and Mohammad H. Elnagdi*

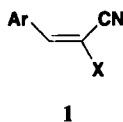
*Department of Chemistry, Faculty of Science, University of Kuwait
P. O. Box 5969 Safat, 13060 KUWAIT*

Some time ago, we reported an efficient synthesis of 2-amino-4H-naphthopyran-3-carbonitriles and of 2-aminobenzo[b]pyran-3-carboxylates *via* reacting 2-naphthol and phenols with arylidene-malononitrile.^{1a,b} The reported biological activity of these derivatives^{2a,b} has stimulated considerable interest in this synthetic approach and several papers describing its utility for synthesis of 2-aminobenzo[b]pyrans and 2-amino-naphtho[1,2-b]pyrans have been published in last few years.^{3a,b,4} In light of this and as a part of an effort aimed at exploring potential biological activity of benzopyrans,⁵ we have investigated the reactivity of a variety of α,β -unsaturated nitriles and α,β -unsaturated ketones toward phenolic derivatives.

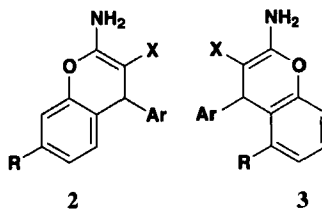
Although the products of the reaction of resorcinol with **1a,b** had been described as **2a,b**,^{1a} Abdel-Latif⁶ apparently unaware of these results, assigned the structure **3a** for the product obtained from resorcinol with a mixture of benzaldehyde and malononitrile (*in situ* generation of **1a**). In order to confirm structure **2a**, we reinspected the ¹H NMR of products of the reaction of resorcinol with **1a,b**. In each case, 4H-pyran, OH, NH₂ signals were observed in the ¹H NMR pattern in addition to the ethyl ester signal of the product of the reaction involving **1b**. In the aromatic region, two doublets appeared at δ 6.42 - 6.53, a singlet at δ 6.9 and a 5-proton signal at δ 7.0-7.19 were observed; the product of the reaction with **1a** shows a similar ¹H NMR pattern [two doublets at δ 6.52-6.72, a singlet at δ 6.81 and a 5-proton signal at δ 7.10-7.24]. These data clearly indicate that the products are **2a,b** since a completely different pattern would have been observed for **3** in the aromatic region.

The reaction of **1c** with resorcinol has afforded **2c**. Compounds **1a** and **1b** reacted similarly with 3-methoxyphenol and with 3-aminophenol in ethanolic piperidine to yield the pyran derivatives **2d-g**. When **1b** was treated with 3-aminophenol in xylene in presence of sodium hydride, **4** was formed in a good yield. It is thus believed that **4** is the thermodynamic product whereas **2g** is the kinetic one.

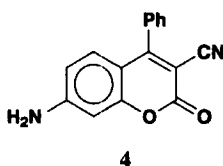
8-Hydroxyquinoline (**5**) also reacted with **1a** in ethanolic piperidine to yield the corresponding 2-amino-4H-pyrano[3,2-h]-quinoline derivative **6a**. While **5** failed to react with ethyl benzylideneacyanoacetate (**1b**) under similar conditions to yield **6b**, when the reaction was conducted



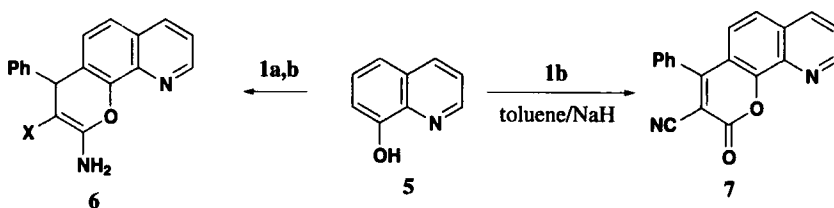
- a) X = CN; Ar = C₆H₅
 b) X = CO₂Et; Ar = C₆H₅
 c) X = CO₂Et; Ar = 4-CH₃OC₆H₄
 d) X = CN; Ar = 4-CH₃OC₆H₄
 e) X = CSNH₂; Ar = 4-CH₃OC₆H₄



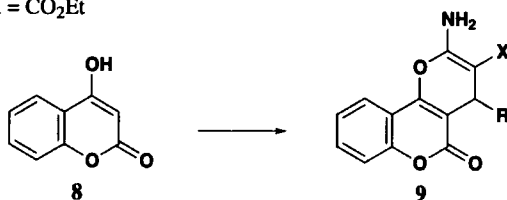
- a) R = OH; Ar = C₆H₅; X = CN
 b) R = OH; Ar = C₆H₅; X = CO₂Et
 c) R = OH; Ar = 4-CH₃OC₆H₄; X = CO₂Et
 d) R = OCH₃; Ar = C₆H₅; X = CN
 e) R = OCH₃; Ar = C₆H₅; X = CO₂Et
 f) R = NH₂; Ar = C₆H₅; X = CN
 g) R = NH₂; Ar = C₆H₅; X = CO₂Et



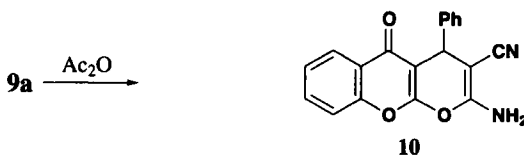
in refluxing pyridine, the pyranoquinoline derivative **6b** was obtained, in contrast to the reported failure of ethyl benzylidenecyanoacetate to add to 1-naphthol under similar conditions.^{2a,b} When **5** was heated with **1b** in toluene and in presence of sodium hydride, the pyranoquinoline derivative **7** was formed. 4-Hydroxycoumarin (**8**) also reacted with **1a,b** to yield the pyranocoumarins **9a,b**. Refluxing **9a** with acetic anhydride resulted in rearrangement into **10**. Compound **8** also reacted with a mixture of acetaldehyde and malononitrile to yield **9c**, a reaction assumed to proceed *via* initial formation of ethylidenemalononitrile which then adds to **8**. A similar reaction sequence has been proposed earlier to account for the formation of aminobenzopyrans from the reaction of phenols with a mixture of acetaldehyde and malononitrile⁷.



- a) X = CN b) X = CO₂Et

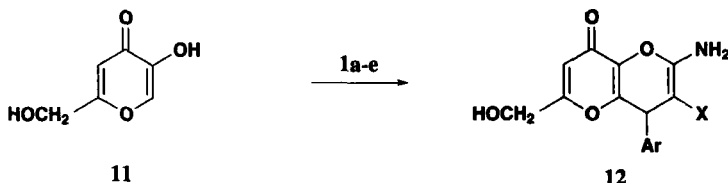


- a) R = C₆H₅; X = CN b) R = C₆H₅; X = CO₂Et c) R = CH₃; X = CN



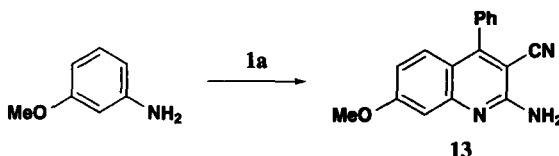
CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES AND OF 2-AMINOQUINOLINE-3-CARBONITRILES

Kojic acid (**11**) also reacted with **1a-d** in refluxing ethanolic piperidine to yield **12a-d**, respectively, in good yields. Similarly the reaction of **11** with 4-methoxybenzylidenecyanothioacetamide **1e** afforded **12e**.

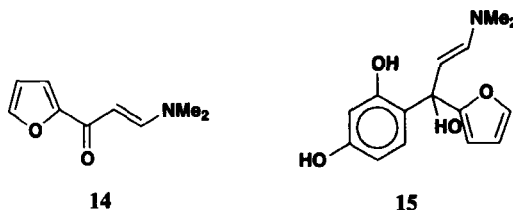


- a) Ar = C₆H₅; X = CN b) Ar = C₆H₅; X = CO₂Et
 c) Ar = 4-CH₃OC₆H₄; X = CO₂Et d) Ar = 4-CH₃OC₆H₄; X = CN
 e) Ar = 4-CH₃OC₆H₄; X = CSNH₂

Although aminoazoles are known to add **1a,b** to afford azolo-pyrimidines,^{8,9} the reaction of aromatic amines with **1a,b** has not been reported. Although, in our hands **1a,b** failed to add to aniline under a variety of conditions, 3-methoxyaniline reacted with **1a** in refluxing xylene in the presence of sodium hydride to yield the quinoline derivative **13** in good yield.



Enaminone **14** has recently been extensively utilized in synthesis of heterocycles.^{5,10a,b} The course of reaction of enaminones with polydentate nucleophiles has been shown to depend on applied conditions.^{5,11} Thus, whereas malononitrile reacted with **14** at reflux in the presence of NaOEt to yield products of initial addition at C-3, the reaction of **14** with the same reagent, at room temperature, afforded the product of attack at C-1. In the present study, treatment of **14** with resorcinol in refluxing ethanol afforded a 1:1 adduct. ¹H NMR of the reaction product indicated that neither olefinic protons nor OH functions were involved in the reaction. This product was thus assigned structure **15**.



EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were recorded on a Shimadzu IR-740 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC-80 spectrometer with DMSO-d₆ as solvent and TMS as an internal standard. Elemental analysis was performed on LECO CHNS 932.

TABLE 1. Analytical Data and Physical Characteristics of New Compounds

Cmpd	Molecular Formula (M. wt)	mp. (°C)	Color ^a	Yield (%)	Elemental Analysis (Calcd)		
					C	H	N
2a	C ₁₆ H ₁₂ N ₂ O ₂ (264)	234-236	colorless	60	72.53 (72.72)	4.57 (4.54)	10.45 (10.61)
2b	C ₁₈ H ₁₇ NO ₄ (311)	219-221	colorless	65	69.31 (69.45)	5.30 (5.47)	4.59 (4.50)
2c	C ₁₉ H ₁₉ NO ₅ (341)	191-194	colorless	40	66.61 (66.86)	5.50 (5.57)	4.20 (4.10)
2d	C ₁₇ H ₁₄ N ₂ O ₂ (278)	196-198	Pale yellow	40	73.50 (73.38)	4.99 (5.04)	10.02 (10.07)
2e	C ₁₉ H ₁₉ NO ₄ (325)	159-162	colorless	40	69.95 (70.15)	5.86 (5.85)	4.34 (4.31)
2f	C ₁₆ H ₁₃ N ₃ O (263)	233-236	pale yellow	70	72.79 (73.00)	4.96 (4.94)	16.14 (15.97)
2g	C ₁₈ H ₁₈ N ₂ O ₃ (310)	180-183	pale yellow	40	69.47 (69.68)	5.66 (5.81)	9.19 (9.03)
4	C ₁₆ H ₁₀ N ₂ O ₂ (262)	272-275	Yellow ^b	42	73.16 (73.28)	4.01 (3.82)	10.60 (10.69)
6a	C ₁₉ H ₁₃ N ₃ O (299)	256-258	gray	60	76.10 (76.25)	4.52 (4.35)	13.93 (14.05)
6b	C ₂₁ H ₁₈ N ₂ O ₃ (346)	299-302	pale yellow	62	72.80 (72.83)	5.00 (5.20)	8.24 (8.09)
7	C ₁₉ H ₁₀ N ₂ O ₂ (298)	255-258	pale yellow	60	76.44 (76.51)	3.50 (3.36)	9.24 (9.40)
9a	C ₁₉ H ₁₂ N ₂ O ₃ (316)	260-262	Pale ^c yellow	60	72.29 (72.15)	3.80 (3.80)	8.91 (8.86)
9b	C ₂₁ H ₁₇ NO ₅ (363)	199-201	Pale yellow	72	69.50 (69.42)	4.80 (4.68)	3.74 (3.86)
9c	C ₁₄ H ₁₀ N ₂ O ₃ (254) (dec.)	226-228	Pale yellow	48	66.18 (66.14)	4.08 (3.94)	11.01 (11.02)
10	C ₁₉ H ₁₂ N ₂ O ₃ (316)	250-252	Pale yellow	62	72.09 (72.15)	3.90 (3.80)	8.66 (8.86)
12a	C ₁₆ H ₁₂ N ₂ O ₄ (296)	231-233	colorless	56	64.80 (64.86)	4.02 (4.05)	9.54 (9.46)
12b	C ₁₈ H ₁₇ NO ₆ (343)	201-205	colorless	36	62.76 (62.97)	4.95 (4.96)	3.87 (4.08)
12c	C ₁₉ H ₁₉ NO ₇ (373)	173-175	colorless	28	61.14 (61.13)	5.02 (5.09)	3.63 (3.75)
12d	C ₁₇ H ₁₄ N ₂ O ₅ (326)	225-227	Pale yellow	41	62.32 (62.57)	4.42 (4.29)	8.33 (8.58)
12e ^d	C ₁₇ H ₁₆ N ₂ O ₅ S (360) (dec.)	233-236	Pale ^c yellow	28	56.54 (56.66)	4.34 (4.44)	7.56 (7.77)
13	C ₁₇ H ₁₃ N ₃ O (275)	170-172	brown	65	73.88 (74.18)	5.00 (4.73)	15.30 (15.27)
15	C ₁₅ H ₁₇ NO ₄ (275)	133-135	yellowish brown	50	65.27 (65.45)	6.10 (6.18)	5.02 (5.09)

a) From EtOH unless otherwise stated. b) From toluene. c) From methanol. d) S, Found: 9.03, Calcd: 8.88.
e) From DMF-EtOH

Reaction of Cinnamitriles (1) with Substituted Phenols and/or Kojic Acid. General Procedure.- A solution of **1** (0.01 mol) in absolute ethanol (30 mL) was refluxed with 3-methoxyphenol (0.01 mol), 3-aminophenol (0.01 mol), resorcinol (0.01 mol), **5**, **8**, and **11** in the presence of piperidine for 3-4 h. Upon being allowed to cool to room temperature, the product precipitated and was collected and recrystallized.

7-Amino-4-phenylcoumarin-3-carbonitrile (4).- A mixture of 3-amino-phenol (0.01 mol) and ethyl benzylideneacyanoacetate (**1b**) (0.01 mol) was refluxed in xylene (20 mL) in the presence of sodium hydride (0.01 mol) for 3 h. The reaction mixture was then allowed to cool to room temperature and the solid product was collected and recrystallized (cf. Tables 1 and 2 for physical and spectral data).

TABLE 2. Spectral Data of Newly Synthesized Compounds

Cmpd	¹ H NMR (δ : ppm)	¹³ C NMR (δ = ppm)	IR (cm ⁻¹)
2a	9.64 (s, 1H, OH); 6.52-7.24 (m, 8H, aromatic); 6.42 (s, 2H, NH ₂); 4.6 (s, 1H, H-4 pyran)	—	3485-3205 (OH, NH ₂); 3070 (CH aromatic); 2165 (CN)
2b	9.53 (s, 1H, OH); 7.54 (s, 2H, NH ₂); 6.42-7.19 (m, 8H, aromatic); 4.78 (s, 1H, H-4 pyran); 3.81-4.08 (q, 2H, CH ₂); 0.95-1.13 (t, 3H, CH ₃)	—	3410-3295 (OH, NH ₂); 3020 (CH aromatic); 2985 (CH aliphatic) 1650 (CO)
2c	7.03-7.34 (m, 7H, aromatic); 6.48-7.17 (s, 2H, NH ₂); 4.81 (s, 1H, H-4 pyran); 3.88-4.05 (q, 2H, CH ₂); 3.69 (s, 3H, OCH ₃); 1.02-1.12 (t, 3H, CH ₃)	169.3 (CO ₂ Et), 158.3 (C-2) 78.2 (C-3), 41.9 (C-4), 128.6 (C-5), 112.0 (C-6), 113.9 (C-7), 157.6 (C-8a), 158.3, 150.0, 141.7, 130.2, 129.1, 128.6 (aromatic), 55.7 (OCH ₃), 59.0 (CH ₂), 14.45 (CH ₃)	3405-3290 (OH, NH ₂); 2970 (CH aliphatic); 1650 (CO)
2d	6.58-7.32 (m, 8H, aromatic); 4.71 (s, 1H, H-4 pyran); 4.52 (s, 2H, NH ₂); 3.84 (s, 3H, OCH ₃)	—	3455-3185 (NH ₂); 3075 (CH aromatic); 2180 (CN)
2e	7.37 (s, 2H, NH ₂); 6.57-7.22 (m, 8H, aromatic); 4.85 (s, 1H, H-4 pyran); 3.83-4.10 (q, 2H, CH ₂); 3.72 (s, 3H, OCH ₃); 0.95-1.14 (t, 3H, CH ₃)	—	3410-3300 (NH ₂); 3050 (CH aromatic); 2925 (CH aliphatic); 1667 (CO)
2f	6.26-7.27 (m, 10H, NH ₂ + aromatic); 5.01 (s, 2H, NH ₂); 4.52 (s, 1H, H-4 pyran)	—	3435-3305 (2NH ₂ 's); 3050 (CH aromatic); 2165 (CN)

TABLE 2. Continued...

Cmpd	¹ H NMR (δ : ppm)	¹³ C NMR (δ = ppm)	IR (cm ⁻¹)
2g	7.55 (s, 2H, NH ₂); 6.25-7.26 (m, 8H, aromatic); 5.15 (s, 2H, NH ₂); 4.76 (s, 1H, H-4 pyran); 3.79-3.97 (q, 2H, CH ₂); 0.94-1.12 (t, 3H, CH ₃)	—	3410-3215 (2NH ₂ 's); 3050 (CH aromatic); 2939 (CH aliphatic); 1659 (CO)
4	7.58 (s, 5H, aromatic); 7.04 (s, 2H, NH ₂); 6.52-6.98 (m, 3H, aromatic)	—	3455-3250 (NH ₂); 2220 (CN); 1697 (CO)
6a	6.71-7.14 (m, 10H, aromatic + quinoline protons); 7.03 (s, 2H, NH ₂); 4.92 (s, 1H, 4 pyran)	—	3450-3300 (NH ₂); 3045 (CH aromatic); 2180 (CN)
6b	7.14-7.63 (m, 10H, aromatic + quinoline protons); 7.01 (s, 2H, NH ₂); 4.12- 4.32 (q, 2H, CH ₂); 1.16-1.31 (t, 3H, CH ₃)	161.8 (CO ₂ Et), 154.9 (C-2), 133.2 (C-3), 42.0 (C-4), 130.0 (C-5), 136.0 (C-6), 138.1 (C-7), 148.1 (C-8), 153.2 (C-9), 130.7, 129.3, 128.8, 127.5, 121.8, 115.4 (aromatic), 62.4 (CH ₂), 14.0 (CH ₃)	3429-3185 (NH ₂); 3055 (CH aromatic); 1714 (CO)
7	7.22-7.92 (m, aromatic + quinoline protons)	164.0 (C-2), 151.9 (C-3), 116.9 (CN), 137.1-123.5 (14 signals; aromatic)	3095 (CH aromatic); 2210 (CN); 1713 (CO)
9a	7.32-7.92 (m, 9H, aromatic + coumarin protons); 4.45 (s, 1H, H-4 pyran); 3.28 (s, 2H, NH ₂)	158.5 (C-2), 104.0 (C-3), 41.0 (C-4), 206.6 (C-5), 151.7 (C-6), 127.9 (C-7), 123.0 (C-8), 143.8 (C-9), 116.9 (CN), 133.2, 128.8, 128.0, 127.5, 124.9, 113.5 (aromatic)	3450-3300 (NH ₂); 2210 (CN); 1681 (CO)
9b	7.14-7.9 (m, 9H, aromatic + coumarin protons); 5.63 (s, 2H, NH ₂); 4.78 (s, 1H, H-4 pyran); 3.71-3.92 (q, 2H, CH ₂); 0.95-1.12 (t, 3H, CH ₃)	167.7 (CO), 161.9 (C-5), 152.8 (C-2), 77.7 (C-3), 42.0 (C-4), 154.9, 145.1, 131.5, 128.0, 127.1, 126.0, 124.2 (aromatic)	3400-3295 (NH ₂); 3050 (CH aromatic); 1681 (CO)
9c	7.32-7.89 (m, 4H, aromatic); 7.07 (s, 2H, NH ₂); 3.20-3.50 (q, 1H, H-4 pyran); 1.27-1.35 (d, 3H, CH ₃)	—	3300-3180 (NH ₂); 3060 (CH aromatic); 2915 (CH aliphatic); 2165 (CN); 1696 (CO)
10	7.31-7.82 (m, 9H, aromatic + coumarin protons); 6.83 (s, 2H, NH ₂); 4.46 (s, 1H, H-4 pyran)	158.2 (C-2), 104.3 (C-3), 42.0 (C-4), 159.5 (C-5), 116.5 (CN), 152.3-122.6 (12 signals; aromatic)	3450-3170 (NH ₂); 2210 (CN); 1695 (CO)

CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES AND OF 2-AMINOQUINOLINE-3-CARBONITRILES

TABLE 2. Continued...

Cmpd	¹ H NMR (δ : ppm)	¹³ C NMR (δ = ppm)	IR (cm ⁻¹)
12a	7.34 (s, 5H, aromatic); 7.20 (s, 2H, NH ₂); 6.33 (s, 1H, H-7); 5.65 (t, 1H, OH); 4.79 (s, 1H, H-4); 4.13-4.20 (d, 2H, CH ₂)	—	3372-3314 (OH); 3198 (NH ₂); 2198 (CN); 1646 (CO)
12b	7.80 (s, 2H, NH ₂); 7.22-7.32 (m, 5H, aromatic); 6.35 (s, 1H, H-7); 5.69-5.74 (t, 1H, OH); 4.81 (s, 1H, H-4); 3.89-4.34 (m, 4H, 2CH ₂); 0.96-1.03 (t, 3H, CH ₃)	—	3420 OH); 3301 (NH ₂); 3060 (CH aromatic); 2988 (CH aliphatic); 1682 (CO ring); 1664 (CO ester)
12c	7.75 (s, 2H, NH ₂); 6.91-7.08 (q, 4H, aromatic); 6.31 (s, 1H, H-7); 5.59-5.84 (t, 1H, OH); 4.74 (s, 1H, H-4); 3.90-4.31 (q+d, 4H, 2CH ₂); 3.71 (s, 3H, OCH ₃); 1.04-1.13 (t, 3H, CH ₃)	—	3380 (OH); x 3266 (NH ₂); 3072 (CH aromatic); 2984, 2938 (CH aliphatic); 1683 (CO ring); 1665 (CO ester)
12d	6.88-7.27 (m, 6H, aromatic + NH ₂); 6.33 (s, 1H, H-7); 5.66 (t, 1H, OH); 4.73 (s, 1H, H-4); 4.14-4.21 (d, 2H, CH ₂); 3.75 (s, 3H, OCH ₃)	—	3420-3280 (OH); 3191 (NH ₂); 2962 (CH aliphatic); 2193 (CN); 1649 (CO ring); 1632 (CO ester)
12e	6.83-7.25 (q, 4H, aromatic); 6.63 (s, 2H, NH ₂); 6.32 (s, 1H, H-7); 5.69-5.73 (t, 1H, OH); 5.14 (s, 1H, H-4); 4.18-4.25 (d, 2H, CH ₂); 3.72 (s, 3H, OCH ₃); 3.32 (NH ₂)	—	3427-3315 (OH, NH ₂); 3159 (NH ₂); 2982 (CH aromatic); 1664 (CO)
13	7.32-7.54 (m, 8H, aromatic); 6.42 (s, 2H, NH ₂); 3.53 (s, 3H, OCH ₃)	—	3440-3205 (NH ₂); 3045 (CH aromatic); 2920 (CH aliphatic); 2210 (CN)
15	9.11 (s, 2H, 2OH); 7.61-7.78 (d, 2H, OH + olefinic); 6.55-7.12 (m, 3H, aromatic); 6.12-6.24 (m, 3H, furan protons); 5.57-5.72 (d, 1H, olefinic); 2.99 (bs, 6H, N(Me) ₂)	—	3340-3030 (OH's + CH aromatic)

Ethyl 2-Amino-4-phenyl-4H-pyrano[3,2-h]quinoline-3-carboxylate (6b).- A solution of 8-hydroxyquinoline (5) (0.01 mol) in pyridine (20 mL) was refluxed with ethyl benzylidenecyanoacetate (1b) (0.01 mol) for 3 h. The reaction mixture was triturated with water. The solid product, so formed, was collected by filtration and recrystallized.

2-Oxo-4-phenyl-4H-pyrano[3,2-h]quinoline-4-carbonitrile (7).- A mixture of 8-hydroxyquinoline (5) (0.01 mol) and (1b) (0.01 mol) was refluxed in toluene (20 mL) in the presence of sodium hydride (0.01 mol) for 5 h. The reaction mixture was evaporated and the remaining product was triturated with

ethanol. The solid product, so formed, was collected by filtration and recrystallized.

Ethyl 2-Amino-4-phenyl-4H-pyrano[3,2-c]coumarin-3-carboxylate (9b).- A solution of (8) (0.01 mol) in toluene (20 mL) was refluxed with 1b (0.01 mol) in the presence of sodium hydride (0.01 mol) for 4 h. The reaction mixture was evaporated and the remaining product was triturated with ethanol. The solid product, so formed, was collected by filtration and recrystallized.

2-Amino-4-methyl-4H-pyrano[3,2-c]coumarin-3-carbonitrile (9c).- A solution of each of acetaldehyde (0.01 mol) and malononitrile (0.01 mol) in ethanol (30 mL) was treated with (8) (0.01 mol) in the presence of piperidine for 3 h, then allowed to cool to room temperature. The solid product, so formed, was collected and recrystallized.

2-Amino-5-oxo-4-phenyl-4H,5H-pyrano[2,3-b]benzo[b]pyran-3-carbonitrile (10).- A solution of (9a) (0.01 mol) in acetic anhydride (20 mL) was refluxed for 3 h. The reaction mixture was evaporated and the remaining product was triturated with water. The solid product, so formed, was collected by filtration and recrystallized.

2-Amino-7-methoxy-4-phenylquinoline-3-carbonitrile (13).- A mixture of 3-methoxyaniline (0.01 mol) and (1a) (0.01 mol) was refluxed in xylene (20 mL) in the presence of sodium hydride (0.01 mol) for 5 h. The reaction mixture was evaporated and the residue was triturated with ethanol. The solid product, so formed, was collected by filtration and recrystallized.

1-(2-Furyl)-1-(2,4-dihydroxyphenyl)-3-N,N-dimethylaminopropenol (15).- A mixture of resorcinol (0.01 mol) and the enaminone (14) (0.01 mol) was refluxed in ethanol (30 mL) in the presence of piperidine for 3 h, then left to cool. The solid product, so formed, was collected by filtration and recrystallized.

Acknowledgment.- This work has been funded by Kuwait University through Research grant SC 080. We are also grateful to Chemistry Department Analab facility at Faculty of Science, University of Kuwait for analytical and spectral data.

REFERENCES

1. a) A. A. Elagamy, S. Z. Sawellim, F. M. A. El-Taweel and M. H. Elnagdi, *Collec. Czech. Chem. Commun.*, **53**, 1534 (1988); b) A. A. Elagamy, F. M. A. El-Taweel, S. Z. A. Sowellim, M. A. Sofan and M. H. Elnagdi, *ibid.*, **55**, 524 (1990).
2. a) M. Brunavs, C. P. Dell, P. T. Gallagher, W. M. Owton and C. W. Smith, *European Patent Appl.* EP557075; *Chem. Abstr.*, **120**, 106768t (1994); b) J. Bloxham, C. P. Dell and C. W. Smith, *Heterocycles*, **38**, 399 (1994).
3. a) N. Martin, A. Martinez-Grau, C. Seoane, J. L. Marco, A. Albert and F. H. Cano, *J. Heterocyclic. Chem.*, **33**, 27 (1996); b) N. Martin, A. Martinez-Grau, C. Seoane and J. L. Marco, *ibid.*, **32**, 1225 (1995).
4. A. A. Elagamey, F. A. A. El-Taweel, M. N. M. Khodeir and M. H. Elnagdi, *Bull. Chem. Soc. Jpn*, **66**, 464 (1993).

CONDENSED 2-AMINO-4H-PYRAN-3-CARBONITRILES AND OF 2-AMINOQUINOLINE-3-CARBONITRILES

5. F. Al-Omran, N. Al-Awadhi, M. M. A. Khalik, K. Kaul, A. A. El-Khair and M. H. Elnagdi, *J. Chem. Res.*, (S) 84; M 603 (1997).
6. F. Abdel-Latif, *Gazz. Chim. Ital.*, **121**, 9 (1991).
7. M. H. Elnagdi, N. H. Taha, F. A. H. Abdellal, R. M. A. Motaleb and F. F. Mahmoud, *Coll. Czech. Chem. Commun.*, **54**, 1082 (1989).
8. A. El-Enzi, B. Al-Saleh and M. H. Elnagdi, *J. Chem. Res.*, (S) 4; (M) 10 (1997).
9. H. A. El-Fahham, F. M. Abdel-Galil, Y. R. Ibrahim and M. H. Elnagdi, *J. Heterocycl. Chem.*, **20**, 667 (1983).
10. a) F. Al-Omran, M. M. A. Khalik, A. A. El-Khair and M. H. Elnagdi, *Synthesis*, 91 (1997); b) S. M. Al-Mousawi, K. Kaul, M. A. Mohammad and M. H. Elnagdi, *J. Chem. Res.*, (S) 318; (M) 2026 (1997).
11. F. Al-Omran, N. Al-Awadi, A. A. El-Khair and M. H. Elnagdi, *Org. Prep. Proced. Int.*, **29**, 285 (1997).

(Received February 17, 1999; in final form April 26, 1999)