Cyclohex-2-en-1-ones in Heterocyclic Synthesis: Facile Synthesis of 5,6-Dihydrocoumarins, their Thio Analogues and their Corresponding Dehydrogenated Derivatives

G. A. M. Nawwar*, B. M. Haggag, and El-S. M. A. Yakout
National Research Centre, Dokki, Cairo, Egypt
Z. Naturforsch. 47b, 1639–1646 (1992); received March 4, 1992
5,7-Disubstituted-4-hydroxycoumarins, Lawesson Reagent, Dehydrogenation, Tetrachloro-o-benzoquinone

Novel synthesis of 5,6-dihydrocoumarins, thioanalogues and their corresponding dehydrogenated derivatives utilizing substituted cyclohex-2-en-1-ones as starting components is reported.

Introduction
Polysubstituted cyclohex-2-en-1-ones are versatile reagents which have been utilized in heterocyclic synthesis [1, 2]. As a part of our programme aimed at developing new, efficient procedures for the synthesis of biologically interesting heterocyclic compounds, using readily obtainable materials, we have previously reported several new approaches for the synthesis of pyrans, azoles, azines and their condensed derivatives [3–6]. In conjunction to this work, we report here simple approaches for the synthesis of polysubstituted dihydrocoumarins, their thio analogues as well as their corresponding dehydrogenated compounds utilizing the cyclohex-2-en-1-ones (1a–d).

Results and Discussion
On heating the 6-acetylcyclohex-2-en-1-ones (1a,b) with diethyl carbonate in toluene in the presence of sodium, the reactions afforded, the corresponding 5,6-dihydro-4-hydroxycoumarins (2a,b). Structure 2 was supported by IR and 1H NMR spectra; the latter exemplified by the 1H NMR spectrum of 2a which revealed the absence of the acetyl group and showed three aliphatic signals at 3.1, 3.2 and 4.5 ppm integrated each to one proton and assigned respectively to the axial methylene proton, the equatorial methylene proton and the methine proton of the CH₂-CH-moiety. This behaviour of the cyclohex-2-en-1-ones (1a,b) towards diethyl carbonate was found to be parallel to that of the o-hydroxyacetophenone derivatives [7].

It is worth to mention that when the reaction of 1a was carried out in presence of 10 mol equivalents of diethyl carbonate instead of 3 mol equivalents, ethyl 5,7-di-(2-thienyl)-5,6-dihydro-4-hydroxycoumarin-3-carboxylate (3a) was obtained. Its 1H NMR showed a triplet at 1.1 ppm (J = 7 Hz) and a quartet at 4.1 ppm (J = 7 Hz) attributable to the ethoxycarbonyl group protons, along with a proton pattern similar to that detected in the spectra of compounds 2. Moreover, the IR spectrum of 3a showed an additional carbonyl group absorption at 1710 cm⁻¹ assigned to the ethoxycarbonyl group beside the previously detected one at 1745 cm⁻¹ in structure 2.

Similarly, derivative 3b could be obtained on reacting 1b with 10 mol equivalents of diethyl carbonate under experimental conditions similar to those used for the preparation of 3a.

The formation of 3a,b is assumed to proceed via the intermediacy of the corresponding dihydrocoumarins (2a,b) with subsequent acylation by diethyl carbonate at the C-3; similar acylation by diethyl carbonate has been previously reported [8].

In order to prepare the corresponding dehydrogenated coumarins, 3,5-di-(2-thienyl)-cyclohex-2-en-1-ones (1c) was acetylated in acetic anhydride/pyridine to afford the ethyl-5,6-dihydroacetylsalicylate derivative (4) in a good yield. When compound 4 was reacted with 1 mol equivalent of tetrachloro-o-benzoquinone in toluene (cf. [5]), the acetoxybenzoate (5) was obtained beside o-tetrachlorocatechol. Structure 5 was established on the basis of spectral data. Its 1H NMR revealed the

* Reprint requests to Dr. G. A. M. Nawwar.
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absence of non-aromatic protons, except the ethyl and methyl protons and showed instead the salicyl 3,5-H as two doublets located at 7.4 and 7.6 (J = 3 Hz) ppm. Its chemical behaviour was also in favour of the given structure. Thus, it could undergo self-cyclization on heating at 240 °C in paraffin oil in the presence of an equimolecular amount of sodium metal affording the corresponding 5,7-di-(2-thienyl)-4-hydroxycoumarin (6). Structure 6 was in accordance with the spectral data (cf. [5]).

In order to simplify this method of dehydrogenation, the cyclohexenone derivative (1c) was reacted with tetrachloro-o-benzoquinone directly. However, the reaction afforded a complex mixture. On repeating the same experiment with (1d), a product was obtained showing in its \(^1\)H NMR spectrum the presence of the ethoxy aliphatic protons, the absence of the aliphatic signals corresponding to the CH\(_2\)–CH moiety detected in the acetyl derivative (4) and appeared instead three aliphatic proton signals located at 5.3 (d, 1H, J = 3 Hz), 6.1 (dd, 1H, \(J_1 = 7\) Hz, \(J_2 = 3\) Hz) and 6.7 (d, 1H, \(J = 7\) Hz) ppm. These data along with elemental analyses and IR could be interpreted on the basis of structure 8.

The formation of 8 is assumed to proceed via the initial dehydrogenation of 1d affording the intermediate 7 and tetrachlorocatechol (as detected by TLC and FeCl\(_3\) test) followed by a 1:8 cycloaddition reaction of another mole of tetrachloro-o-benzoquinone on 7 to give the 1:1 adduct 8. Similar proposals concerning the cycloaddition reactions of tetrachloro-o-benzoquinone and vinylfurans have been previously reported [5, 9].

On allowing the salicyl derivative (8) to react with acetic anhydride followed by a subsequent heating at 240 °C in paraffin oil in the presence of sodium metal, a new 5,7-disubstituted-4-hydroxy-
coumarin derivative (9) was obtained. Structure (9) was given for the product based on analytical and spectral data (cf. Experimental).

To prepare the thio analogues of compounds 2a,b, thiation of the cyclohexenones (1c,d) with phosphorus pentasulphide was first tested but failed. However, Lawesson reagent succeeded to thiate derivative (1c) affording a product with a molecular formula C_{17}H_{16}OS_{4} (m/z 364) which was identified as the cyclohex-2-en-l-thione (10a). Its IR spectrum revealed the absence of the two carbonyl absorptions previously detected in the starting compound 1c and showed instead the C=S absorptions (cf. Experimental).

A similar result was obtained from the reaction of compound 1d with Lawesson reagent affording the dithiocyclohex-2-ene structure (10b). Compound 10a could be cyclized with malononitrile in the presence of sodium hydride to afford the 3-cyano-5,7-dihydrothiocoumarin derivative (12a). The IR spectrum of 12a showed carbonyl and cyano group absorptions at 1720 cm\(^{-1}\) and 2200 cm\(^{-1}\), respectively; it also showed an SH absorption at 3450 cm\(^{-1}\). Moreover, the \(^1\)H NMR spectrum showed an aliphatic proton pattern similar to that obtained for its 5,6-dihydro-4-hydroxy-coumarin analogue (2a).

An analogous result was obtained on applying the same reaction to derivative 10b and accordingly the dihydrothiocoumarin (12b) was obtained.

In an attempt to prepare new cyclohexenone derivatives, 1-(2-hydroxy-3-methoxyphenyl)-3-(3,4-dichlorophenyl) propenone (13a) was reacted with ethyl acetoacetate (cf. preparation of 1a-d [10]). However, the reaction afforded a product with a molecular formula C_{25}H_{25}NO_{4}Cl_{2} (m/z 474) and its \(^1\)H NMR revealed the characteristic piperidine protons pattern [11]. On these bases as well as IR and elemental analyses, the N-acyl piperidine structure (14a) was established for this product rather than the aimed cyclohexenone or 3-acetyl-4-(3,4-dichlorobenzoxyethyl)-8-methoxy-3,4-dihydrocoumarin which would be expected according to previous reports [12].

A parallel result was obtained on applying the same reaction to derivative 13b affording so (14b). Compounds 14a,b were thought to be formed via the initial formation of the aimed cyclohexenones which further reacted with piperidine present in the media as catalyst. However, when the reaction of 13a with ethylacetoacetate was carried out in the presence of triethylamine instead of piperidine, a mixture of two products was obtained which was separated by fractional crystallization.
The product, m.p. 265 °C, with molecular formula \( C_{20}H_{14}O_4Cl_2 \) (m/z 389) was identified as the benzo[c]coumarin (15a) (cf. Experimental). On the other hand, the second product obtained was identified as the aimed cyclohexenone derivative (16a) based on elemental and spectral data.

Similarly, compounds 15b and 16b could be obtained from the reaction of the propenone derivative (13b) with ethyl acetoacetate in the presence of triethylamine.

In addition, when the benzocoumarin derivative (15a) was boiled under reflux in dioxane in presence of an equimolecular amount of piperidine, the reaction afforded the corresponding N-acyl-piperidine (14a).

It is assumed that benzocoumarins (15a, b) were produced via the self cyclization of 16 evolving the phenolic OH and the ethoxycarbonyl group; similar proposal has been previously reported [13].

Thus, some polysubstituted coumarins which are not readily accessible are now available through simple procedures and seem interesting for biological activity evaluation.

**Experimental**

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. IR (KBr) were recorded with a Pye-Unicam SP-1000 spectrometer. \(^1\)H NMR spectra were run in DMSO on a GEMINI-200 spectrometer, using TMS as an internal reference. Mass spectra were recorded at 70 eV with a Varian MAT 311A mass spectrometer. Elemental analyses were performed by the Central Service Laboratory in the National Research Centre.

Cyclohexenones (1a–d) were prepared according to reported method [10].

**5-Heteroaryl-7-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin (2a, b)** and ethyl 5-heteroaryl-7-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin-3-carboxylate (3a, b). General procedure

To a solution of each of the cyclohexenones (1a, b) (0.01 mol) in toluene (20 ml), molecular sodium (0.02 mol or 0.07 mol) was added followed by diethyl carbonate [(3.8 g, 0.03 mol) or (11.8 g, 0.1 mol)] and the reaction mixture was heated at 90 °C for 3 h. After cooling, the solution was extracted with water (2 portions, each 20 ml) and the aqueous layer was acidified with dilute hydrochloric acid. The product, thus formed, was collected and crystallized.

**5,7-Di-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin (2a)**

Yellow crystals from ethanol. Yield 40%; m.p. 180 °C.

\[ C_{17}H_{12}O_3S_2 \] (328.40)

Calcd C 62.17 H 3.68 S 19.52%,

Found C 62.00 H 3.63 S 19.14%.

IR (KBr) \( \nu \): 1745 (CO), 1646 (CO).

**Ethyl 5,7-di-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin-3-carboxylate (3a)**

Yellowish white crystals from toluene. Yield 60%, m.p. 77 °C.

\[ C_{20}H_{16}O_5S_2 \] (400.459)

Calcd C 59.98 H 4.03 S 16.01%,

Found C 59.81 H 3.87 S 15.90%.

IR (KBr) \( \nu \): 3425 (OH), 1745 (CO), 1715 (CO), 1660 (CO).

**5-(2-Furyl)-7-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin (2b)**

Brown crystals from ethanol. Yield 45%; m.p. 165 °C.

\[ C_{17}H_{13}O_3S \] (312.34)

Calcd C 65.37 H 3.87 S 10.26%,

Found C 65.25 H 3.59 S 9.99%.

IR (KBr) \( \nu \): 1745 (CO), 1650 (CO). \(^1\)H NMR: 3.1 (1 H, m, coumarin H-6 axial), 3.2 (1H , m, coumarin H-6 equatorial), 4.5 (1 H, m, coumarin H-5), 6.6 (4H , m, coumarin H-3, H-8, furan H-3 and H-4), 7.1 (2H , m, thiophene H-3 and H-4), 7.6–7.8 (2H , m, thiophene H-5 and furan H-5), 14.1 (1 H, brs, OH).

**Ethyl 5-(2-furyl)-7-(2-thienyl)-4-hydroxy-5,6-dihydrocoumarin-3-carboxylate (3b)**

Yellowish white crystals from toluene. Yield 55%, m.p. 73 °C.

\[ C_{20}H_{16}O_6S \] (384.399)

Calcd C 62.49 H 4.19 S 8.34%,

Found C 62.34 H 4.00 S 8.10%.

IR (KBr) \( \nu \): 3420 (OH), 1755 (CO), 1715 (CO), 1660 (CO).
Ethyl 4,6-di- (2-thienyl) -5,6-dihydroacetylsalicylate (4)

Compound 1c was acetylated according to reported method [5] to give white crystals from ethanol. Yield 70%, m.p. 105 °C.

\[ C_{19}H_{18}O_4S_2 \] (374.47)
Calcd C 60.94 H 4.84 S 17.12%,
Found C 60.73 H 4.69 S 16.85%.

IR (KBr) v: 1770 (CO acetyl), 1695 (CO ester).

\[ ^1H \text{ NMR: 1.1 (3H, t, CH}_3 \text{ ethoxy) 2.1 (3H, s, acet} \text{yl CH}_3 \text{), 3.0 (1H, m, cyclohexene methylene axial}
\text{proton), 3.2 (1H, m, cyclohexene methylene equatorial proton), 4.0 (2H, q, O–CH}_2 \text{), 4.5 (1H, m, cyclohexene methine}
\text{proton), 6.4 (1H, m, cyclohexene H-3), 7.0–7.5 (4H, m, H-3 and H-4 of both thiophene), 7.7–7.8 (2H, m, H-5 of both}
\text{thiophene).} \]

Ethyl 4,6-di- (2-thienyl) acetylsalicylate (5)

Compound 4 was dehydrogenated with tetrachloro-o-benzoquinone following the reported method [5] affording yellow crystals crystallizable from cyclohexane. Yield 55%, m.p. 110 °C.

\[ C_{19}H_{16}O_4S_2 \] (372.45)
Calcd C 61.27 H 4.33 S 17.21%,
Found C 61.12 H 4.23 S 16.96%.

IR (KBr): 1770 (CO acetyl), 1690 (CO ester).

\[ ^1H \text{ NMR: 1.1 (3H, t, CH}_3 \), 2.1 (3H, s, CH}_3 \text{ acetyl), 4.3 (2H, q, O–CH}_2 \text{), 7.1 (2H, m, 2 thiophene H-3), 7.4 (1H, d, J}_{3,5} = 3
\text{Hz, salicylate H-3), 7.6 (1H, d, J}_{5,3} = 3 \text{Hz, salicylate H-5), 7.8–7.9 (4H, m, H-3 and H-4 of both thiophene), 7.7–7.8 (2H, m, H-5 of both}
\text{thiophene).} \]

The salicylate (5) was cyclized following the reported method [5] to give yellow crystals crystallizable from cyclohexane. Yield 20%, m.p. 118 °C.

\[ C_{17}H_{10}O_6S_2 \] (326.38)
Calcd C 62.56 H 3.08 S 19.64%,
Found C 62.60 H 3.00 S 19.38%.

IR (KBr): 3410 (OH), 1730 (CO), 1620 (CO).

\[ ^1H \text{ NMR: 5.8 (1H, d, J = 3 Hz, furan H-3), 6.1 (1H, dd, J}_1 = 7 \text{Hz, J}_2 = 3 \text{Hz, furan H-4), 6.8 (1H, d, J = 7 Hz, furan}
\text{H-5), 7.1–8.1 (6H, m, thiophene and coum} \text{arin H-3, H-6 and H-8), 11.3 (1H, s, OH).} \]

Ethyl 4- (2-thienyl) -6- (5,6,7,8-tetrachloro-3a,9a-dihydrofuro[2,3-b][1,4] benzodioxin-2-yl) salicylate (8)

The propenone (1d) was dehydrogenated with tetrachloro-o-benzoquinone following the reported method [5] to give colourless crystals from dioxane. Yield 40%, m.p. 210 °C.

\[ C_{23}H_{10}O_8S_4Cl_4 \] (560.23)
Calcd C 49.30 H 2.51 S 5.72 Cl 25.31%,
Found C 49.26 H 2.37 S 5.45 Cl 25.00%.

IR (KBr): 3460 (OH), 1760 (CO).

\[ ^1H \text{ NMR: 1.1 (3H, t, CH}_3 \text{), 4.2 (2H, q, OCH}_2 \text{), 5.7 (1H, d, J = 3 Hz, furan H-3), 6.1 (1H, dd, J}_1 = 7 \text{Hz, J}_2 = 3
\text{Hz, furan H-4), 6.7 (1H, d, J = 7 Hz, furan H-5), 7.1 (2H, m, thiophene H-3 and salicylate H-3), 7.3 (1H, d, J = 4 Hz, salicylate H-5), 7.6}
(2H, m, thiophene H-4 and H-5).} \]

5- (5,6,7,8-Tetrachloro-3a,9a-dihydrofuro-[2,3-b][1,4]benzodioxin-2-yl)-7- (2-thienyl)-4-hydroxycoumarin (9)

Compound 8 (2.8 g, 0.005 mol) was boiled under reflux with acetic anhydride (20 ml) in presence of a catalytic amount of pyridine (1 ml) for 3 h. The reaction mixture was then cooled, poured onto crushed ice to give the acetyl derivative as an oily mass which was dissolved in toluene (30 ml) and dried over sodium sulfate anhydrous. To the toluene solution, molecular sodium and paraffin oil were added and the mixture was heated at 240 °C according to the reported method [5]. The solid product, obtained was collected and crystallized from dioxane to give pale yellow crystals. Yield 50%, m.p. 255 °C.

\[ C_{23}H_{10}O_8S_4Cl_4 \] (556.20)
Calcd C 49.66 H 1.81 S 5.76 Cl 25.49%,
Found C 49.41 H 1.63 S 5.39 Cl 25.20%.

IR (KBr): 3430 (OH), 1740 (CO).

\[ ^1H \text{ NMR: 5.8 (1H, d, J = 3 Hz, furan H-3), 6.1 (1H, dd, J}_1 = 7 \text{Hz, J}_2 = 3 \text{Hz, furan H-4), 6.8 (1H, d, J = 7 Hz, furan H-5), 7.1–8.1 (6H, m, thiophene and coum} \text{arin H-3, H-6 and H-8), 11.3 (1H, s, OH).} \]

5-(Heteroaryl) -3- (2-thienyl) -6-thioethoxycyclohex-2-en-1-thione (10a,b). General procedure

A mixture of each of the cyclohexenones (1c,d) (0.01 mol) and Lawesson reagent (4.04 g, 0.01 mol) was boiled under reflux in dry benzene (30 ml) for 4 h. The reaction mixture was evaporated under vacuum and the residue was dissolved in chloroform (2 ml). The desired fraction was separated by column chromatography (silica gel) using acetone: pet. ether 60–80 (1:9).
3,5-Di(2-thienyl)-6-thioethoxycyclohex-2-en-1-thione (10a)

Yellow crystals. Yield 40%, m.p. 75 °C.

C₁₇H₁₆O₈S₄ (364.56)
Calcd C 56.00 H 4.42 S 35.18%,
Found C 56.03 H 4.25 S 34.99%.

IR (KBr) ν: 1270 (C=S), 1245 (C=S).

5-(2-Furyl)-3-(2-thienyl)-6-thioethoxycyclohex-2-en-1-thione (10b)

Red crystals. Yield 40%, m.p. 70 °C.

C₁₇H₁₆O₂S₃ (348.49)
Calcd C 58.58 H 4.62 S 27.60%,
Found C 58.61 H 4.20 S 27.46%.

IR (KBr) ν: 1265 (C=S), 1245 (C=S).

1H NMR δ: 1.2 (3H, t, CH₃), 2.8-3.2 (2H, m, methylene protons in the cyclohexene), 3.7-4.1 (3H, m, O-CH₂ and methine H-5), 4.3 (1H, d, J = 12 Hz, methine H-6), 6.4 (1H, d, J = 3 Hz, cyclohexene H-2), 6.6 (2H, dd, furan H-3, H-4), 7.0-7.8 (4H, m, furan H-5 and thiophene protons).

3-Cyano-5-(2-furyl)-7-(2-thienyl)-4-thiol-5,6-dihydrothiocoumarin (12b)

Brown crystals from dioxane. Yield 40%, m.p. > 300 °C.

C₁⁸H₁⁰N₂O₅S₄ (369.47)
Calcd C 58.51 H 3.00 N 3.79 S 26.03%,
Found C 58.34 H 2.84 N 3.54 S 25.87%.

IR (KBr) ν: 3400 (SH), 2200 (CN), 1715 (CO).

3-(Aryl)-5-(2-hydroxy-3-substituted phenyl)-6-(N-carboxypiperidinyl)-cyclohex-2-en-1-one (14a, b).

General procedure

Method I

Ethyl acetoacetate (1.3 g, 0.01 mol) was boiled under reflux with an equimolecular amount of each of the propenones (13a, b) in ethanol (30 ml) in presence of piperidine (0.84 g, 0.01 mol) for 6 h. The reaction mixture was then concentrated, cooled and the solid product obtained was collected and crystallized.

Method II

The benzocoumarin (15a) (3.9 g, 0.01 mol) was boiled under reflux in dioxane (30 ml) in presence of piperidine (0.84 g, 0.01 mol) for 3 h. The reaction mixture was then concentrated, water was added till precipitation commenced. The product obtained was filtered off and crystallized.

3-Cyano-5-(2-heteroaryl)-7-(2-thienyl)-4-thiol-5,6-dihydrothiocoumarin (12a, b). General procedure

To a solution of each of compounds 10a, b (0.01 mol) in toluene (30 ml), sodium hydride (0.24 g, 0.01 mol) was added with stirring for 15 minutes. Malononitrile (0.99 g, 0.015 mol) was then added and the solution was boiled under reflux for 6 h. The reaction was then extracted with water, the aqueous phase acidified with dilute hydrochloric acid and the product obtained was collected and crystallized.

3-Cyano-5,7-di(2-thienyl)-4-thiol-5,6-dihydrothiocoumarin (12a)

Brown crystals from dioxane. Yield 40%, m.p. > 300 °C.

C₁₈H₁₅N₂O₅Cl₂ (474.36)
Calcd C 63.29 H 5.31 N 2.95 Cl 14.94%,
Found C 63.00 H 5.25 N 2.73 Cl 14.65%.

IR (KBr) ν: 3500 (OH), 1675 (CO), 1655 (CO).

1H NMR δ: 1.5 (6H, s, SH), 3.2-3.4 (6H, m, cyclohexene methylene protons and 2N-methylene group protons in piperidine), 3.7 (3H, s, O-CH₃), 3.8-3.9 (1H, m, cyclohexene H-5), 5.1 (2H, m, cyclohexene H-2 and H-6), 7.4-7.7 (6H, m, 2 Ph), 12.1 (1H, s, OH).
3-((2-Furyl)-5-(2-hydroxyphenyl)-6-(N-carboxypiperidinyl)cyclohex-2-en-l-one (14b)

Yellow crystals from ethanol. Yield 35% (Method I), m.p. 198 °C.

\[ C_{22}H_{23}NO_4 (365.42) \]

Calcd C 72.31 H 6.34 N 3.83%,

Found C 72.15 H 6.21 N 3.76%.

IR (KBr) v: 3500 (OH), 1670 (CO), 1650 (CO).

\[ ^1H \text{NMR} : \]

1.6 (6H, m, piperidine), 3.2-3.4 (6H, m, cyclohexene methylene protons and 2N-methylene group protons in piperidine), 3.9-4.0 (1H, m, cyclohexene H-5), 6.2 (2H, m, furan H-3 and H-4), 7.4-7.7 (5H, m, Ph and furan H-5), 12.0 (1H, s, OH).

5-Aryl-10-alkyl-3-hydroxy-[6,6a] dihydrobenzo[c]coumarin (15a, b) and ethyl 3,5-diaryl cyclohex-2-en-l-one-6-carboxylate (16a, b).

General procedure

A mixture of ethyl acetoacetate (1.3 g, 0.01 mol) and each of the propenones (13a, b) (0.01 mol) was boiled under reflux in ethanol (25 ml) in presence of triethylamine (1.1 g, 0.01 mol) for 12 h. The reaction mixture was left to cool and the precipitate formed was filtered off. It was found to be a mixture of 15 and 16 which could be separated by fractional crystallization from ethanol compounds (15) precipitated first then the mother liquor was concentrated to give compounds 16.

5-(3,4-Dichlorophenyl)-10-methoxy-3-hydroxy-[6,6a] dihydrobenzo[c]coumarin (15a)

Brown crystals from ethanol. Yield 50%, m.p. 265 °C.

\[ C_{20}H_{14}O_4Cl_2 (389.29) \]

Calcd C 61.71 H 3.62 Cl 18.21%,

Found C 61.54 H 3.47 Cl 17.94%.

IR (KBr) v: 3425 (H-bonded OH), 1740 (CO), 1676 (CO). \[ ^1H \text{NMR} : \]

3.1 (1H, m, benzocoumarin H-6 axial), 3.3 (1H, m, benzocoumarin H-6 equatorial), 3.6 (3H, s, O-CH$_3$), 4.5 (1H, m, benzocoumarin methine H), 6.3 (1H, m, benzocoumarin H-4), 7.3-7.6 (6H, m, 3,4-dichlorophenyl and ArH), 11.3 (1H, s, H-bonded OH).

3-Hydroxy-5-((2-furyl)-[6,6a] dihydrobenzo[c]coumarin (15b)

Brown crystals from ethanol. Yield 45%, m.p. 254 °C.

\[ C_{17}H_{16}O_5 (280.279) \]

Calcd C 72.85 H 4.31%,

Found C 72.63 H 4.06%.

IR (KBr) v: 3405 (H-bonded OH), 1740 (CO), 1670 (CO). \[ ^1H \text{NMR} : \]

3.2 (1H, m, benzocoumarin H-6 axial), 3.4 (1H, m, benzocoumarin H-6 equatorial), 4.4 (1H, m, benzocoumarin methine H), 6.3 (1H, m, benzocoumarin H-4), 6.5 (2H, m, furan H-3, H-4), 7.4-7.7 (5H, m, furan H-5 and ArH).

Ethyl-3-(3,4-diclorophenyl)-5-((2-hydroxy-3-methoxyphenyl)cyclohex-2-en-l-one-6-carboxylate (16a)

Yellow crystals from ethanol. Yield 30%, m.p. 175 °C.

\[ C_{22}H_{20}O_5Cl_2 (435.29) \]

Calcd C 60.69 H 4.63 Cl 16.29%,

Found C 60.61 H 4.39 Cl 16.02%.

IR (KBr) v: 3450 (OH), 1740 (CO), 1665 (CO). \[ ^1H \text{NMR} : \]

1.3 (3H, t, CH$_3$), 2.7-3.1 (2H, m, methylene protons in the cyclohexenone), 3.5 (3H, s, O-CH$_3$), 3.7-4.1 (4H, m, O-CH$_2$, cyclohexenone H-5 and H-6), 6.3 (1H, d, J = 3 Hz, cyclohexenone H-2), 7.0-7.6 (6H, m, ArH), 11.0 (1H, s, OH).

Ethyl-3-(2-furyl)-5-((2-hydroxyphenyl)cyclohex-2-en-l-one-6-carboxylate (16b)

Yellow crystals from ethanol. Yield 28%, m.p. 152 °C.

\[ C_{19}H_{18}O_5 (326.348) \]

Calcd C 69.92 H 5.55%,

Found C 69.75 H 5.41%.

IR (KBr) v: 3450 (OH), 1740 (CO), 1660 (CO). \[ ^1H \text{NMR} : \]

1.3 (3H, t, CH$_3$), 2.8-3.2 (2H, m, methylene protons in the cyclohexenone), 3.7-4.1 (4H, m, O-CH$_2$, cyclohexenone H-5 and H-6), 6.3 (1H, d, J = 3 Hz, cyclohexene H-2), 7.0-7.7 (7H, m, furan and Ph protons), 11.0 (1H, s, OH).