Electrochemical Synthesis of 4-(Dihydroxyphenylthio)-2*H*-chromen-2-one Derivatives

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The 4-(dihydroxyphenylthio)-2*H*-chromen-2-one derivatives have been synthesized by direct electrochemical oxidation of catechols in the presence of 4-mercaptocoumarin as a nucleophile in water/acetonitrile (50/50) solution, in a one-pot process, at carbon rod electrode, in an undivided cell and in constant current conditions, through an EC mechanism. The products are characterized by spectra data. Besides, the difference in electrochemical oxidation of catechol in the presence of 4-hydroxycoumarin and 4-mercaptocoumarin explained by computational structure, natural bond orbital (NBO) analysis and density functional theory (DFT: B3LYP/6-31G*//B3LYP/6-31G*) based methods, using the GAUSSIAN 98 package of programs.

Key words 4-mercpatocoumarin; electrochemical oxidation; catechol; B3LYP/6-31G*; 4-(3,4-dihydroxyphenylthio)-2*H*-chromen-2-one

The number of natural and synthetic coumarin (2*H*-chromen-2-one) derivatives[1)] have been reported to exert notably antimicrobial[2,3)] as well as antifungal,[4,5)] tuberculostatic[6)] and anti-human immunodeficiency virus (HIV)[7,8)] activity. Moreover, the antibiotic novobiocin belongs to the hydroxycoumarin series. The importance of these compounds have motivated many workers to synthesize a number of them, and numerous methods have been developed for their preparation.[9—11)] On the other hand, catechols are a promising group of compounds worthwhile for further investigation, which may lead to the discovery of selective acting, biodegradable agrochemicals having high human, animal and plant compatibility.[12,13)] A literature survey reveals that, in contrast to the widely studied, coumarin derivatives, no paper has reported the synthesis of 4-(dihydroxyphenylthio)-2*H*-chromen-2-one derivatives. Following our experiences in electrochemical oxidation of catechols in the presence of nucleophiles,[14—21)] we envisaged that synthesis of organic compounds with both structures of catechol and coumarin might cause an enhancement of pharmaceutical properties and medicinal activities. This idea prompted us to investigate the electrochemical oxidation of catechols in the presence of 4-mercaptocoumarin as the nucleophile and we have discovered an easy and one-pot electrochemical method for the synthesis of 4-(dihydroxyphenylthio)-2*H*-chromen-2-one derivatives (**4a**—**d**) in high yield and purity, using this environmentally friendly method with high atom economy. In order to study the feasibility of the electrochemical synthesis of 4-(dihydroxyphenylthio)-2*H*-chromen-2-one derivatives (**4a**—**d**) and mechanistic aspects of this conversions, electrochemical oxidation of catechols in the absence and presence of 4-mercaptocoumarin was studied using cyclic voltammetry. As well, in this work computational studies were used for quantitative answer to the question concerning the difference in electrochemical oxidation of catechol in the presence of 4-hydroxycoumarin and 4-mercaptocoumarin.

Results and Discussion

Electrochemical Studies Figure 1, curve a, shows the voltammetric curve obtained for the oxidation of catechol (1 mM) in water/acetonitrile (50/50) solution containing sodium acetate (c=0.2 M) on a glassy carbon electrode. In the studied potential-range, a well defined voltammetric curve is obtained that has an anodic (A_1) and the corresponding cathodic (C_1) peaks. These peaks are correspond to the oxidation of catechol (**1a**) to *o*-benzoquinone (**2a**) and *vice versa* within a quasi-reversible two electron process.[14—21)] The oxidation of catechol (**1a**) in the presence of 4-mercaptocoumarin (**3**) as a nucleophile was studied in some details. Figure 1, curve b shows the cyclic voltammogram obtained

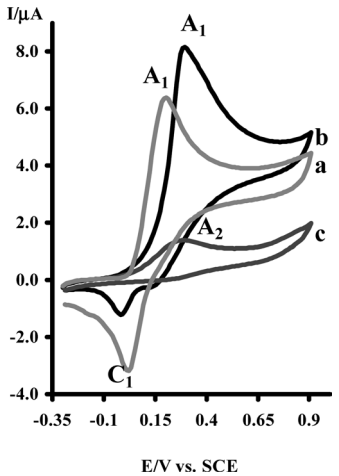

Fig. 1. Cyclic Voltammograms of (a) 1 mM Catechol (**1a**) in the Absence of 4-Mercaptocoumarin (**3**), (b) 1 mM Catechol (**1a**) in the Presence of 1 mM 4-Mercaptocoumarin (**3**) and (c) 1 mM 4-Mercaptocouamrin (**3**) in the Absence of Catechol, at a Glassy Carbon Electrode in Water/Acetonitrile (50/50) Solution Containing Sodium Acetate (c=0.2 M)

Scan rate: 50 mV s^{-1}; t=25±1 °C.

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for a 1 mM solution of **1a** in the presence of 1 mM of 4-mercaptocoumarin (**3**). In this case, the presence of the counterpart cathodic peak strongly depends on the sweep rate (Fig. 2). Thus, for the highest sweep rate employed a well-defined cathodic peak is observed. The peak current ratio ($I_p^{C_1}/I_p^{A_1}$) is lower than one. It is 0.15 for a sweep rate of 50 mV/s, and it increases when the sweep rate increases. A similar situation is observed when the 4-mercaptocoumarin (**3**) to catechol (**1a**) concentration ratio is decreased (Fig. 3). These indicate the reactivity of electrochemically generated *o*-benzoquinone (**2a**) toward **3**. In this figure, curve c is the voltammogram of **3**.

Diagnostic criteria of cyclic voltammetry and the spectroscopic data (IR, ^{1}H-NMR, ^{13}C-NMR and MS) of the isolated products, indicated that the reaction mechanism of electrooxidation of catechol (**1a**) in the presence of 4-mercaptocoumarin (**3**) is EC ('E' represents an electron transfer at the electrode surface, and 'C' represents a homogeneous chemical reaction) (Chart 1).

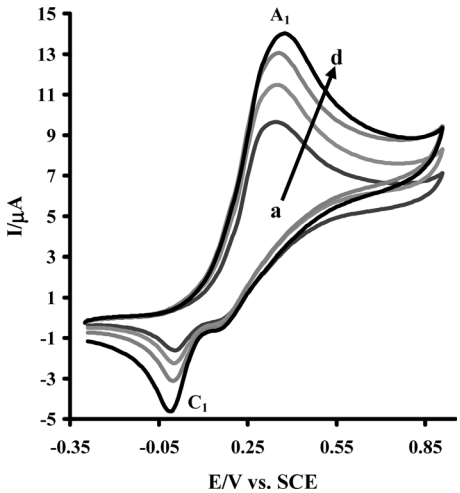


Fig. 2. Typical Cyclic Voltammograms of 1 mM Catechol (**1a**) in the Presence of 1 mM 4-Mercaptocoumarin (**3**), at a Glassy Carbon Electrode, in Water/Acetonitrile (50/50) Solution Containing Sodium Acetate (c=0.2 M), in Various Scan Rates

Scan rate from (a) to (d) are: 25, 35, 45 and 55 mV s^{-1}, respectively.

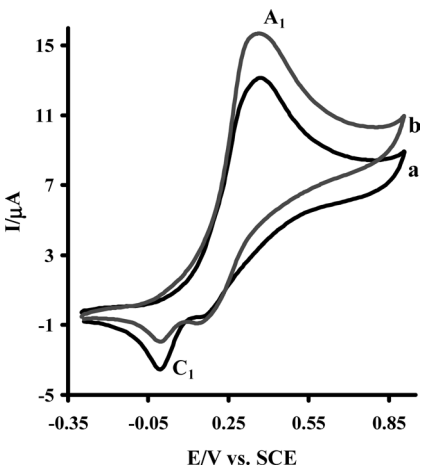


Fig. 3. Cyclic Voltammograms of 1 mM Catechol (**1a**) in the Presence of (a) 1 mM 4-Mercaptocoumarin (**3**), (b) 2 mM 4-Mercaptocoumarin (**3**), at a Glassy Carbon Electrode, in Water/Acetonitrile (50/50) Solution Containing Sodium Acetate (c=0.2 M)

Scan rate: 45 mV s^{-1}; t=25±1 °C.

The increasing of the peak A_1 current in the presence of 4-mercaptocoumarin (**3**) (Fig. 1, curve b) is due to the oxidation of 4-mercaptocoumarin (**3**) which occurred at the same potential as that observed for the oxidation of catechol. Also, the positive shift of the peak A_1 in the presence of 4-mercaptocoumarin (**3**) (Fig. 1, curve b) that was enhanced during the repetitive recycling of potential is probably due to the formation of a thin film of product at the surface of the electrode, inhibiting, to a certain extent, the performance of the electrode process.[14—21] The overoxidation of **4a** was circumvented during the preparative reaction because of the presence of the electron-withdrawing group.

We have previously investigated the electrochemical oxidation of catechols in the presence of 4-hydroxycoumarin (**6**) as a nucleophile.[22] The results signified the formation of benzofuran derivatives (coumestan derivatives) (**9**) *via* inter and intramolecular Micheal addition reactions (ECEC mechanism) with consumption of four electrons per molecule of catechols (Chart 2).

The significant difference in electrochemical oxidation of catechols in the presence of 4-hydroxycoumarin (**6**) and 4-mercaptocoumarin (**3**) is due to the structure of the formed intermediate (**7**) in the case of **6** (Chart 3).

Comparison of the structure of **7** with **4a** and **4d** reveals that in the compound **7**, coumarin group acts as an electron-donating group whereas in compounds **4a** and **4d**, mercaptocoumarin group is an electron-withdrawing group. In this direction, Fig. 4 presents cyclic voltammogram of product **4a** in comparison with catechol. A positive shift in half wave

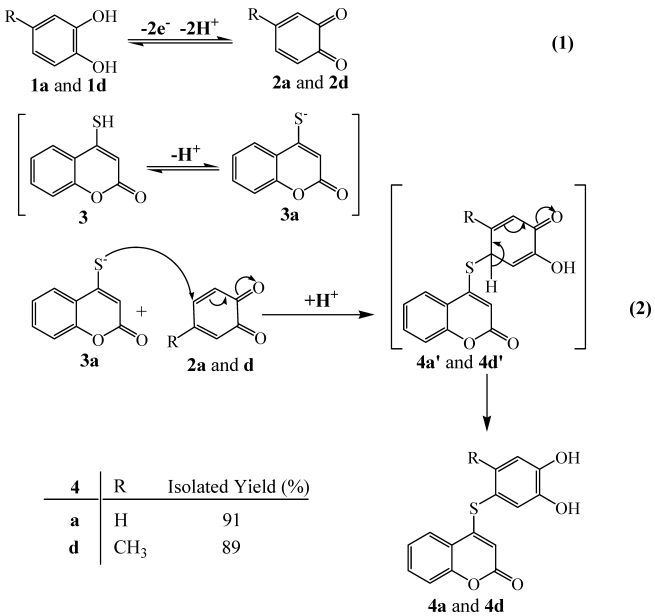


Chart 1

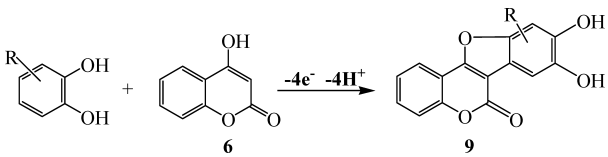


Chart 2

potential ($E_{1/2}$) of **4a** is observed. $E_{1/2}$ was achieved experimentally as midpoint potential between the anodic and cathodic peaks. $E_{1/2}$ for the compound **4a** and catechol are 0.16 and 0.11 V, respectively (Fig. 4). This confirmed that mercaptocoumarin group in compound **4a** is an electron-withdrawing group.

Also, as discussed above, in the electrochemical oxidation of catechols in the presence of 4-hydroxycoumarin (**6**), the C-alkylation proceeds to form the intermediate **7**, and subsequent O-cylization affords the benzofuran derivatives. Whereas, in the presence of 4-mercaptorcoumarin (**3**), S-alkylation proceeds to form the compound **4**. This can be explained using the hard and soft acids and bases (HSAB) concept. According to this concept, hard acids tend to interact with hard bases, while soft acids tend to interact strongly with soft bases. The carbon is a soft electrophile and the RO$^-$ is hard nucleophile whereas RS$^-$ is soft nucleophile.[23] Therefore, hydroxycoumarin reacted with its C atom (soft-nucleophile–soft-electrophile) whereas mercaptocoumarin reacted with S atom (softer-nucleophile).

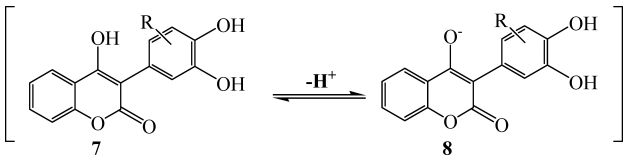


Chart 3

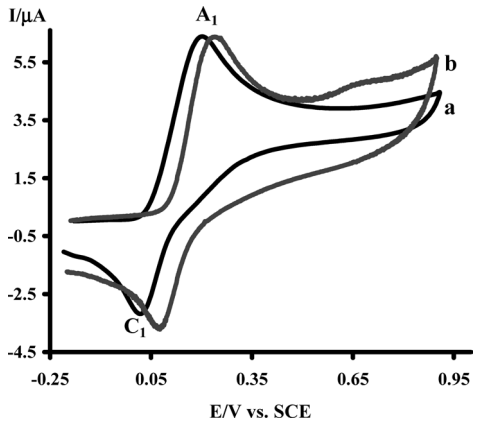


Fig. 4. Cyclic Voltammograms of (a) 1 mM Catechol (**1a**), (b) 1 mM 4-(3,4-Dihydroxyphenylthio)-2*H*-chromen-2-one (**4a**) at a Glassy Carbon Electrode in Water/Acetonitrile (50/50) Solution Containing Sodium Acetate (c= 0.2 M)

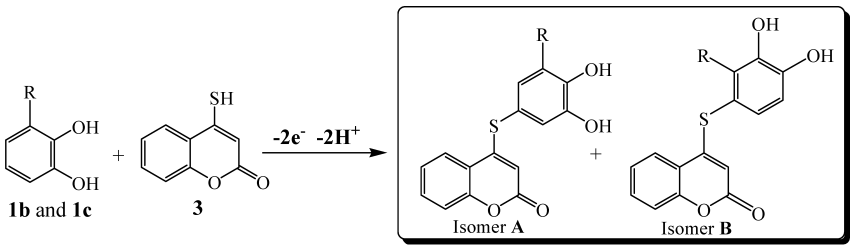
Scan rate: 50 mV s^{-1}; t=25±1 °C.

The electrooxidation of 4-methylcatechol (**1d**), 3-methoxycatechol (**1c**) and 3-methylcatechol (**1b**) in the presence of **3** proceed in a similar way to that of **1a**. The existence of a methyl or methoxy group at the C-3 position of **1b** and **1c** causes the *o*-benzoquinones derived from the oxidation of these catechols (**2b**, **2c**) attacked by **3** from C-4 or C-5 positions to yield two types of product in each case which has been confirmed by ^{1}H-NMR results. So, we suggest that *o*-benzoquinones **2b** and **2c** are attacked from two positions by **3** leading to the formation of the two types of product in each case (isomers A and B) (Chart 4).

A characteristic feature of the electrolysis is that low current density is required. The current efficiency and yield of product decrease with increasing current density. These observations can be explained by the occurrence of back reactions, such as the reduction of *o*-benzoquinones (**2**) on the platinum cathode and side reactions such as oxidation of nucleophile and/or final product (**4**) during constant current electrolysis in an undivided cell. In this work current density 1.5 mA/cm^2 is preferred.

Computational Studies Here, the difference in electrochemical oxidation of catechol in the presence of 4-hydroxycoumarin (**6**) and 4-mercaptocoumarin (**3**) was explained by computational structure, NBO (natural bond orbital) analysis and density functional theory (DFT: B3LYP/6-31G*// B3LYP/6-31G*) based methods, using the GAUSSIAN 98 package of programs. Structural parameters for the ground state of compounds **1a**, **7** and **4a**, were calculated by B3LYP/6-31G* level of theory. These results showed that in the compound **7**, catechol and the substituted rings have the same direction and therefore electronic delocalization of $\pi \rightarrow \pi^*$ occurred between catechol and adjacent rings. But in the compound **4a**, rings are approximately orthogonal together (C_1–S–C_8 angle is 103 degree), and hence the electronic delocalization of $\pi \rightarrow \pi^*$ is stopped and substituted rings attract electrons of catechol ring (Figs. 5, 6).

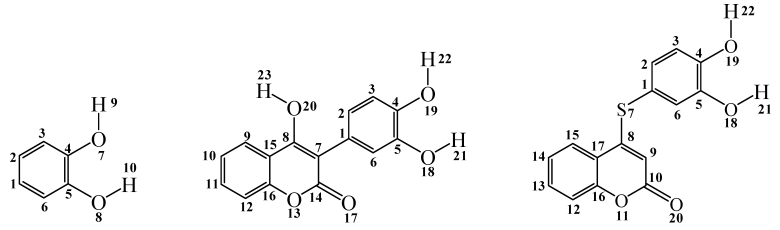
Based on the optimized ground state geometry using B3LYP/6-31G* method, the NBO analysis of donor–acceptor (bond–antibond) interactions revealed that the stabilization energies (E2) associated with the electronic delocalization



4	R	Isolated Yield (%) (Isomers A+B)	Isomer Ratio[a]
b	CH_3	86	52.5/47.5
c	OCH_3	75	96.5/3.5

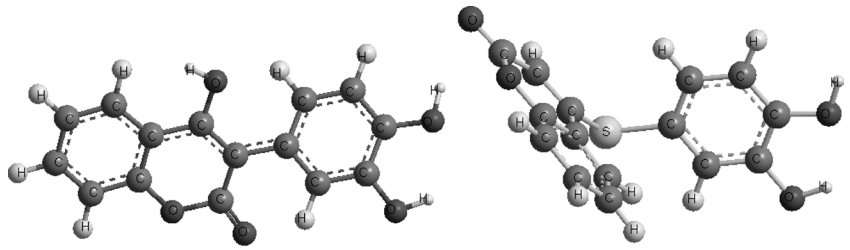
[a]Isomer ratio obtanied from ^{1}H-NMR peak ratio of methyl (for **4b**) and methoxy (for **4c**).

Chart 4



1a **7** **4a**

Fig. 5. Numbering Used for Structure of Compounds **1a**, **7**, and **4a**



7 **4a**

Fig. 6. B3LYP/6-31G* Calculated Structure of Compounds **7** and **4a**

Table 1. NBO Stabilization Energies (E2) of Electronic Delocalization $\pi\rightarrow\pi^*$ Molecular Orbital, Based on the B3LYP/6-31G* Calculated Geometries

Resonance energy	B3LYP/6-31G*		
	Compound **1a**	Compound **7**	Compound **4a**
$\pi_{1-2}\rightarrow\pi^*_{3-4}$	19.58	19.80	—
$\pi_{1-2}\rightarrow\pi^*_{5-6}$	18.71	19.21	—
$\pi_{3-4}\rightarrow\pi^*_{1-2}$	17.89	18.08	—
$\pi_{3-4}\rightarrow\pi^*_{5-6}$	18.22	17.48	—
$\pi_{5-6}\rightarrow\pi^*_{1-2}$	20.24	19.09	—
$\pi_{5-6}\rightarrow\pi^*_{3-4}$	20.36	21.27	—
$\pi_{2-3}\rightarrow\pi^*_{1-6}$	—	—	18.54
$\pi_{1-6}\rightarrow\pi^*_{2-3}$	—	—	18.98
Lp S$\rightarrow\pi^*_{1-6}$	—	—	0.96

Table 2. NBO Calculated Energetic Gap of Frontier Molecular Orbital, Based on the B3LYP/6-31G* Calculated Geometries

Energy	B3LYP/6-31G*		
	Compound **1a**	Compound **7**	Compound **4a**
HOMO	−0.20665	−0.19811	−0.21724
LUMO	0.09807	−0.06221	−0.07289
ΔE	0.21472	0.13590	0.14435

$\pi\rightarrow\pi^*$ molecular orbital decreased in the compound **7** to **4a**. NBO results show that the sum of $\pi\rightarrow\pi^*$ resonance energy in catechol ring of the compounds **7** and **4a** are 114.93 and 38.48 kcal mol^{-1}, respectively (Table 1).

In addition, NBO results are used to study frontier molecular orbitals. Energetic gap of HOMO and LUMO for compounds **1a**, **7** and **4a** showed that this gap of energy for the compound **1a**, **7** and **4a** are 0.21472, 0.13590 and 0.14435, respectively (Table 2).

Decreased gap of energy for the compounds **7** and **4a** against the compound **1a** revealed that the conjugated double bonds in these molecules increased (aromatic substituted groups) against compound **1a** and also showed that conjugation in the compound **7** is very greater than the compound **4a**.

Experimental

Reaction equipments are described in earlier papers.[14—21] All chemicals were reagent-grade materials. Sodium acetate, solvents and reagents were of pro-analysis. These chemicals were used without further purification. 4-Mercaptocoumarin (4-mercapto-2*H*-chromen-2-one) was prepared by the procedure reported previously.[24]

Electroorganic Synthesis A solution (*ca.* 80 ml) of sodium acetate solution (c=0.2 M) in water/acetonitrile (50/50) containing 1 mmol of catechols (**1a**—**d**) and 1 mmol of 4-mercaptocoumarin (**3**) was electrolyzed in an undivided cell equipped with graphite anode (an assembly of four rods with 30 cm^2 area) and a large stainless steel gauze cathode at 25 °C under constant-current density of 1.5 mA/cm^2. The electrolysis was terminated when the anodic peak that corresponds to the oxidation of catechol (**1a**—**d**) (A_1 in Fig. 1) in cyclic voltammetry disappears (after consumption of 2.9 F/mol, current efficiency 69%). The process was interrupted during the electrolysis, and the graphite anode was washed in acetone in order to reactivate it. At the end of electrolysis, to achieve better precipitation, a few drops of acetic acid were added to the solution and the cell was placed in a refrigerator overnight. The solid precipitated was collected by filtration and was washed several times with water.

Characteristic of Products (4a—d). 4-(3,4-Dihydroxyphenylthio)-2*H*-chromen-2-one ($C_{15}H_{10}O_4S$) (4a) mp 245—247 °C (dec.). IR (KBr) cm^{-1}: 3421, 3297, 3048, 1715, 1604, 1548, 1447, 1387, 1341, 1271, 1158, 943, 822, 759, 743, 652. ^{1}H-NMR (300 MHz, acetone-d_6) δ: 5.52 (s, 1H, C_9-H), 7.08 (d, J=1.3 Hz, 2H, aromatic), 7.14 (t, J=1.1 Hz, 1H, aromatic), 7.41 (m, J=7.9 Hz, 2H, aromatic), 7.68 (t, J=8.1 Hz, 1H, aromatic), 7.91 (dd, J=8.1, 1.6 Hz, 1H, aromatic) and 8.66 (broad, 2H, –OH). ^{13}C-NMR (75.4 MHz, DMSO-d_6) δ: 107.9, 115.1, 117.3, 117.4, 118.0, 122.8, 124.0, 124.6, 128.8, 132.9, 147.1, 148.7, 152.7, 158.6, 158.9. MS (EI): m/z (relative intensity): 286 $[M]^{+\cdot}$ (71), 268 (58), 253 (32), 235 (48), 203 (25), 192 (13), 178 (24), 145 (59), 121 (52), 108 (81), 89 (93), 77 (71), 63 (66), 43 (100).

4-(3,4-Dihydroxy-5-methylphenylthio)-2*H*-chromen-2-one (4b) and 4-(3,4-Dihydroxy-2-methylphenylthio)-2*H*-chromen-2-one ($C_{16}H_{12}O_4S$) (5b) (Isomers A and B) mp 257—261 °C (dec.). IR (KBr) cm^{-1}: 374, 2925, 2855, 1718, 1684, 1603, 1547, 1447, 1342, 1290, 1182, 1122, 1024, 943, 844, 820, 759, 743, 706. ^{1}H-NMR (300 MHz, acetone-d_6) δ: 2.28 (s, 3H, methyl), 2.32 (s, 3H, methyl), 5.39 (s, 1H, C_9-H), 5.57 (s, 1H, C_9-H), 6.93 (m, J=8.6 Hz, 1H, aromatic), 7.06 (m, J=8.6 Hz, 1H, aromatic), 7.37 (m, J=9.1 Hz, 2H, aromatic), 7.43 (m, J=9.1 Hz, 2H, aromatic), 7.67 (m, J=2.9 Hz, 2H, aromatic), 7.77 (m, J=2.9 Hz, 2H, aromatic), 7.89 (dd,

J=8.4, 1.7 Hz, 1H, aromatic), 7.96 (dd, J=8.4, 1.7 Hz, 1H, aromatic). ^{13}C-NMR (75.4 MHz, acetone-d_6) δ: 10.8, 13.9, 107.5, 107.9, 114.3, 117.3, 120.2, 124.0, 124.1, 124.6, 128.8, 129.1, 130.2, 131.5, 132.8, 132.9, 133.0, 145.4, 146.1, 146.9 148.0, 152.7, 152.8, 157.8, 158.5, 158.6, 159.0, 167.5. MS (EI): m/z (relative intensity): 300 $[M]^{+\cdot}$ (100), 288 (31), 282 (51), 267 (41), 239 (11), 178 (70), 150 (36), 145 (47), 121 (45), 110 (26), 89 (59), 77 (20), 63 (33).

4-(3,4-Dihydroxy-5-methoxyphenylthio)-2*H*-chromen-2-one ($C_{16}H_{12}O_5S$) (4c) mp 228—230 °C (dec.). IR (KBr) cm^{-1}: 3438, 3176, 2927, 1673, 1599, 1544, 1505, 1343, 1309, 1239, 1196, 1175, 1107, 952, 843, 824, 762. ^{1}H-NMR (300 MHz, acetone-d_6) δ: 3.90 (s, 3H, methoxy), 5.61 (s, 1H, C_9-H), 6.86 (s, 2H, aromatic), 7.41 (m, J=8.8 Hz, 2H, aromatic), 7.70 (m, J=8.5 Hz, 1H, aromatic), 7.91 (dd, J=8.3, 1.6 Hz, 1H, aromatic) and 9.2 (broad, about 2H, –OH). ^{13}C-NMR (75.4 MHz, acetone-d_6) δ: 56.3, 108.0, 111.4, 114.5, 117.2, 117.3, 118.0, 123.9, 124.6, 132.9, 137.4, 147.1, 149.7, 152.7, 158.5, 158.7. MS (EI): m/z (relative intensity): 316 $[M]^{+\cdot}$ (100), 283 (60), 178 (74), 145 (50), 121 (41), 89 (53), 63 (34).

4-(4,5-Dihydroxy-2-methylphenylthio)-2*H*-chromen-2-one ($C_{16}H_{12}O_4S$) (4d) mp 273—275 °C (dec.). IR (KBr) cm^{-1}: 3344, 1686, 1600, 1546, 1519, 1445, 1414, 1344, 1320, 1270, 1187, 1158, 950, 869, 841, 824,767, 743. ^{1}H-NMR (300 MHz, acetone-d_6) δ: 2.29 (s, 3H, methyl), 5.41 (s, 1H, C_9-H), 7.01 (s, 1H, aromatic), 7.10 (s, 1H, aromatic), 7.44 (m, J=8.1 Hz, 2H, aromatic), 7.69 (t, J=9.2 Hz, 1H, aromatic), 7.94 (d, J=8.4 Hz, 1H, aromatic), 8.5 (broad, 2H, –OH). ^{13}C-NMR (75.4 MHz, acetone-d_6) δ: 19.2, 107.3, 113.4, 117.2, 118.1, 118.7, 123.5, 124.2, 124.6, 132.9, 135,6, 145.0, 148.9, 152.9, 157.5, 158.5. MS (EI): m/z (relative intensity): 300 $[M]^{+\cdot}$ (38), 272 (8), 267 (16), 178 (24), 145 (30), 121 (44), 89 (100), 77 (40), 63 (78), 39 (50).

Computational Details DFT (density functional theory) calculations were carried out using B3LYP/6-31G*//B3LYP/6-31G*, level of theory with the GAUSSIAN 98 package of programs[25] implemented on a Pentium-PC computer with a 2.6 GHz processor. Initial estimation of the structural geometry of the compounds **1a**, **7** and **4a** was obtained by a molecular mechanic program PCMODEL (88.0),[26] and for further optimization of geometry, we used the PM3 method of the MOPAC 7.0 computer program.[27,28] The GAUSSIAN 98 package of programs were finally used to perform DFT calculations at the B3LYP/6-31G* level. Energy-minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for the compounds **1a**, **7** and **4a** has been fixed by means of the number of imaginary frequencies. For minimum state structure, only real frequency values, and in the transition-state, only single imaginary frequency values, were accepted.[29,30] NBO analysis was then performed at the B3LYP/6-31G* level by the NBO 3.1 program[31,32] included in the GAUSSIAN 98 package of programs.

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