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3-Acetyl-4-hydroxy-chromen-2-one (**1**) was brominated with phenyltrimethylammonium tribromide to afford 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) whose reactions with thiourea, thioacetamide and ammonium dithiocarbamate gave respectively 3-(2-amino-thiazol-4-yl)-4-hydroxy-, 4-hydroxy-3-(2-phenyl-thiazol-4-yl)- and 4-hydroxy-3-(2-mercapto-thiazol-4-yl)chromen-2-one. In a similar manner, compound **2** was treated with four 1-substituted-2-thioureas and thiobenzamide to give the corresponding 4-hydroxy-3-(thiazol-4-yl)-chromen-2-one derivatives.

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In pharmacology, 2-aminothiazoles are one of the most important compounds as precursors to synthetic drugs, such as sulphathiazole (antibiotic) and thiabendazole (anti-helminthic). The 2-aminothiazoles are prepared by Hantzsch reaction of α -haloketones with thioureas [1-6]. As an extension of 3-acetyl-4-hydroxy-chromen-2-one chemistry [7-8], now we wish to report the preparation of 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) as new synthon and the synthesis of 4-hydroxy-3-(thiazol-4-yl)-chromen-2-ones by its reactions with thioureas, thioamides and ammonium dithiocarbamate.

Results and Discussion.

Preparation of 3-(2-Bromoacetyl)-4-hydroxy-chromen-2-one (**2**).

3-(2-Bromoacetyl)-4-hydroxy-chromen-2-one (**2**) is expected to be a very useful compound for the synthesis of a various heterocycle-substituted chromen-2-ones (coumarins). However, its preparation by using bromine is difficult, since the chromen-2-one nucleus is very susceptible to electrophilic substitution [9-11]. For example, bromination of 3-acetyl-4-hydroxy-chromen-2-one (**1**) in a conventional manner (bromine/acetic acid) gave substitution products at the aromatic nucleus as a major product [12-15]. Then, we carried out bromination by using phenyltrimethylammonium tribromide [16-19], which is a useful reagent for α -bromination of ketones and acetals.

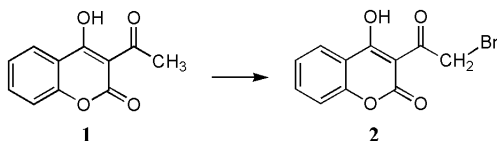


Figure 1

When 3-acetyl-4-hydroxy-chromen-2-one (**1**) was treated with phenyltrimethylammonium tribromide in tetrahydrofuran to give only 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) as yellow crystals (mp 144-146°). Its structure was determined from the spectral data as well as elemental analysis ($C_{11}H_7BrO_4$). In the ir spectrum, three characteristic absorptions were observed at 3185 (OH), 1725 (bromoacetyl C=O) and 1685 cm^{-1} (chromen-2-one C=O). The 1H nmr spectrum shows a singlet peak at δ 4.28 (2H) for CH_2 , signals at δ 7.31-7.67 (4H) for ring protons and broadened singlet peak at δ 15.70 (OH).

Synthesis of 4-Hydroxy-3-(thiazol-4-yl)coumarines.

Treatment of 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) with thiourea in refluxing ethanol for 30 minutes gave 3-(2-amino-thiazol-4-yl)-4-hydroxy-chromen-2-one hydrobromide (**3a**) as yellow needles (mp 255-257°) in a 60% yield. Its structure was determined on the basis of the spectral data as well as on elemental analysis ($C_{12}H_8N_2O_3S \cdot HBr$). The ir spectrum shows three characteristic absorptions at 3381 (OH), 3120 (NH_2) and 1693 cm^{-1} (C=O). In the 1H nmr spectrum, one isolated signal is observed at δ 7.46 (s) for 5'-H, besides multiplet peaks at δ 7.29-7.82 (4H), for aromatic protons, broadened singlet peak at δ 15.87 for hydroxyl proton and singlet peak at δ 8.58 for NH_2 protons. R_f value for this compound is 0.25 using methyl-ethyl ketone:toluene, 1:9 (v/v), as eluent. Compound **3a** also gave positive coloration with iron(III) chloride solution.

The reaction of **2** with 1-(methyl)thiourea gave 4-hydroxy-3-(2-methylamino-thiazol-4-yl)-chromen-2-one (**3b**) ($C_{13}H_{10}N_2O_3S$), in 67 % yield (mp 218-220°). The methylamino group was confirmed from the 1H nmr spectrum, which shows a singlet peak at δ 2.98 (3H) for methyl group and a broad peak at δ 11.01 (1H) for the NH proton.

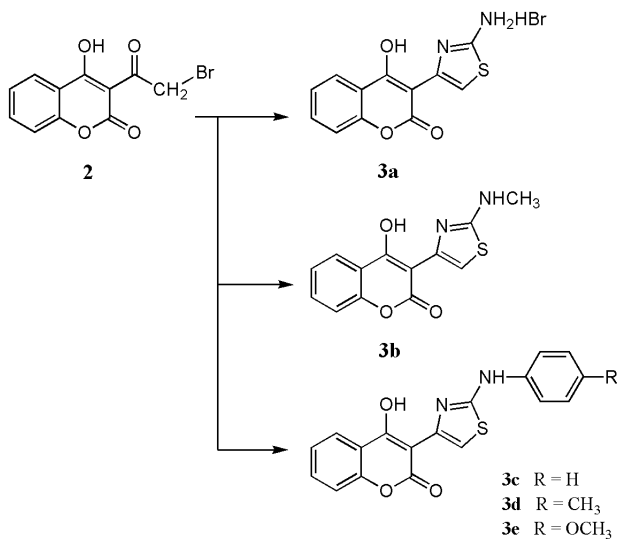


Figure 2

In this spectrum, one isolated singlet is observed at δ 7.38 for 5'-H, besides multiplet peaks at δ 7.29-7.84 (4H), for aromatic protons and a broadened peak at δ 16.36 for the OH proton. R_f value for this compound is 0.42 (methyl-ethyl ketone:toluene, 1:9, v/v)

In a similar manner, treatment of **2** with three 1-(aryl)thioureas gave the corresponding 3-(2-aryl-thiazol-4-yl)-chromen-2-ones (**3c-e**) in 63-74 % yields. These structures were also determined from the spectral data and elemental analysis (See: Experimental).

When a mixture of **2** and thioacetamide in ethanol was refluxed, 4-hydroxy-3-(2-methyl-thiazol-4-yl)-chromen-2-one (**4a**) (C₁₃H₉NO₃S) was isolated as yellow needles in a 72% yield (mp 182-184°). Its structure was determined from the spectral data and elemental analysis. In the ir spectrum, two characteristic absorptions were observed at 3378 (OH), and 1697 (C=O) cm⁻¹. In the ¹H nmr spectrum, one isolated singlet is observed at δ 8.28 for 5'-H, besides multiplet peaks at δ 7.29-7.80 (4H) for aromatic

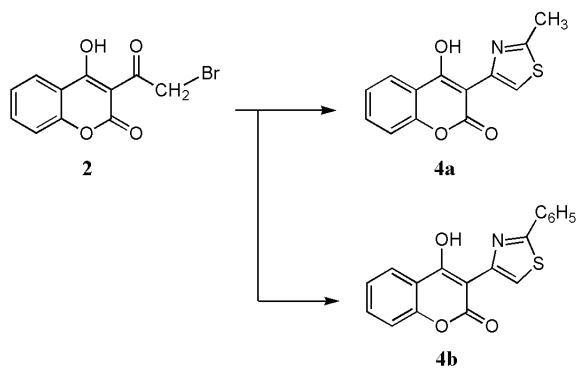


Figure 3

protons, peak at δ 2.46 (3H) for CH₃ group, and a broad peak at δ 15.36 for OH.

Compound **2** was also reacted with thiobenzamide to afford the corresponding 4-hydroxy-3-(2-phenyl-thiazol-4-yl)-chromen-2-one (**4b**), in 74% yield (mp 189-191°). The structure of this product was confirmed from its spectral data (See: Experimental).

Furthermore, compound **2** was heated with ammonium dithiocarbamate in refluxing ethanol to give 4-hydroxy-3-(2-mercapto-thiazol-4-yl)-chromen-2-one (**5**) (mp 204-206°) in a 81 % yield. R_f value for this compound is 0.42 (methyl-ethyl ketone:toluene, 1:9, v/v).

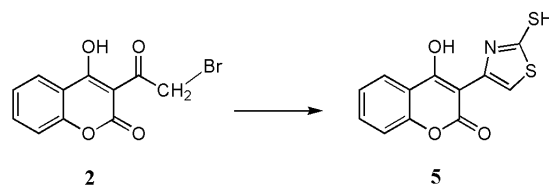


Figure 4

In its ¹H nmr spectrum, the SH and 5'-H protons were observed at δ 3.46 (s) and 8.23 (s), respectively. The elemental analysis (C₁₂H₇NO₃S₂) also supported the structure.

In summary, it is found that 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) is useful material for the synthesis of heterocycle-substituted 4-hydroxy coumarin compounds.

Some of 4-hydroxy-3-(thiazol-4-yl)-chromen-2-one derivatives (as a *N*[5-(4-hydroxy-chromen-2-one)-thiazol-2'-yl]-benzenesulphamide [20]) are readily prepared and expected to be pharmaceutical precursors.

EXPRIMENTAL

Measurements.

Melting points were recorded on a Kofler-hot stage apparatus and are uncorrected. Microanalysis of carbon, hydrogen and nitrogen was carried out with a Carlo Erba 1106 microanalyser. The ir spectra were run on Perkin-Elmer Grating Spectrophotometers Model 137 and Model 197. The nmr spectra were recorded on a VARIAN FT 80 A and 200" Gemini spectrometer, in CDCl₃ and DMSO-d₆, using TMS as the internal standard. Chemical shifts are given in δ (ppm); J, coupling constants in hertz (Hz), abbreviations: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet and br-broadened). Thin layer chromatography was taken on plastic sheets of silica gel 60 (Merck). Abbreviations used: PhTAPBr₃-phenyltrimethylammonium tribromide, DMSO-dimethylsulphoxide-d₆, EtOH-ethanol, CDCl₃-deuteriochloroform, r.t.-room temperature.

Starting Compound: 3-Acetyl-4-hydroxy-chromen-2-one (**1**).

To a solution of 4-hydroxy-chromen-2-one (3 g, 18.6 mmoles) in acetic acid (16 ml) phosphorous oxychloride (5.6 ml) was added. The mixture was heated at reflux for 30 minutes. After cooling, the precipitate was collected and recrystallized from ethanol, to give 3-acetyl-4-hydroxy-chromen-2-one (**1**), as white needles, in a yield of 2.7 g (90%), mp 134-136°; ir (KBr): 3185, 2950, 1700, 1705, 1610, 1560, 1460, 1310, 1130, 950, 840, 820, 770 cm^{-1} ; ^1H nmr (200 MHz, CDCl_3): δ 2.43 (s, 3H, CH_3), 7.35 (ddd, 1H, 6-H, $^3J_{6,5}=7.8$ Hz, $^4J_{6,8}=1.2$ Hz, $^3J_{6,7}=7.4$ Hz), 7.42 (dd, 1H, 8-H, $^3J_{7,8}=8.35$ Hz, $^4J_{6,8}=1.2$ Hz), 7.42 (ddd, 1H, 7-H, $^3J_{7,8}=8.35$ Hz, $^3J_{7,6}=7.4$ Hz, $^4J_{7,5}=1.6$ Hz), 7.69 (dd, 1H, 5-H, $^3J_{5,6}=7.8$ Hz, $^4J_{5,7}=1.6$ Hz), 15.7 (OH); ^{13}C nmr (50 MHz, CDCl_3): δ 28.33 (CH_3), 160.10 (CO), 177.32 (C-4), 116.91 (C-8), 159.65 (C-2), 154.10 (C-9), 136.85 (C-7), 116.09 (C-5), 124.82 (C-6), 114.41 (C-10), 101.91 (C-3); ms: m/z 204 (M⁺, 100) 189 (74), 161 (43), 120 (17), 119 (31), 92 (56), 78 (33), 43 (28).

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{O}_4$: C, 64.71; H, 3.95. Found: C, 64.92; H, 3.68.

3-(2-Bromoacetyl)-4-hydroxy-chromen-2-one (**2**).

To a solution of 3-acetyl-4-hydroxy-chromen-2-one (**1**) (2.0 g, 9.8 mmoles) in tetrahydrofuran (40 ml) was added phenyltrimethylammonium tribromide (3.68 g, 9.8 mmoles) in a period of 15 minutes (at room temperature). A precipitate was deposited from the solution, and the color of the solution changed into pale yellow. After stirring for 20 minutes and standing for 30 minutes, cold water (100 ml) was added to the reaction mixture. The precipitate was collected, washed with water and recrystallized from ethanol to afford 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) as light yellow needles, in yield 2.51g (90%), mp 144-146°; ir (KBr): 3185, 1725, 1685, 1560, 1437, 1200, 1032, 945, 842, 822, 771 cm^{-1} ; ^1H nmr (200 MHz, CDCl_3): δ 4.28 (s, 2H, CH_2), 7.31 (ddd, 1H, 6-H, $^3J_{6,5}=7.38$ Hz, $^4J_{6,8}=1.16$ Hz, $^3J_{6,7}=7.32$ Hz), 7.39 (dd, 1H, 8-H, $^3J_{7,8}=8.35$ Hz, $^4J_{6,8}=1.16$ Hz), 7.42 (ddd, 1H, 7-H, $^3J_{7,8}=8.35$ Hz, $^3J_{7,6}=7.37$ Hz, $^4J_{7,5}=1.63$ Hz), 7.67 (dd, 1H, 5-H, $^3J_{5,6}=7.89$ Hz, $^4J_{5,7}=1.63$ Hz), 15.70 (OH); ^{13}C nmr (50 MHz, CDCl_3): δ 33.41 (CH_2), 183.50 (CO), 185.32 (C-4), 115.91 (C-8), 158.65 (C-2), 153.00 (C-9), 134.85 (C-7), 125.09 (C-5), 124.82 (C-6), 119.41 (C-10), 100.91 (C-3).

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{BrO}_4$: C, 46.67; H, 2.49. Found: C, 46.92; H, 2.38.

Reactions of 3-(2-Bromoacetyl)-4-hydroxy-chromen-2-one (**2**) with Thioureas.

To a solution of 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (**2**) (1 g, 3.5 mmoles) in absolute ethanol (60 ml) thiourea (3.5 mmoles) was added. The mixture was refluxed for 30 minutes. After cooling, the precipitate was collected and recrystallized from ethanol-10% sodium hydroxide, to give 3-(thiazol-4-yl)-4-hydroxy coumarines (**3a-e**).

3-(2-Amino-thiazol-4-yl)-4-hydroxy-chromen-2-one Hydrobromide (**3a**).

This compound was obtained from the reaction with thiourea as yellow needles (ethanol-10% sodium carbonate) in a yield of 0.71 g (60%), mp 255-257°; ir (KBr): 3433, 3381, 3241, 3120, 1693, 1609, 1524, 1405, 1328, 1294, 1165, 1072, 950 cm^{-1} ; ^1H nmr (200 MHz, DMSO-d_6): δ 7.29-7.37 (m, 2H, 6-H, 8-H,

$^4J_{6,8}=1.16$ Hz, $^3J_{6,5}=7.90$ Hz, $^3J_{6,7}=7.35$ Hz, $^3J_{8,7}=8.35$ Hz), 7.46 (s, 1H, 5'-H), 7.44 (ddd, 1H, 7-H, $^3J_{6,7}=7.35$ Hz, $^4J_{7,5}=1.63$ Hz, $^3J_{8,7}=8.35$ Hz), 7.82 (dd, 1H, 5-H, $^4J_{7,5}=1.63$ Hz, $^3J_{6,5}=7.90$ Hz), 8.58 (bs, 1H, NH_2), 15.87 (s, 1H, OH); ^{13}C nmr (50 MHz, DMSO-d_6): δ 165.42 (C-2'), 140.67 (C-4'), 108.56 (C-5'), 154.28 (C-2), 93.86 (C-3), 163.09 (C-4), 123.76 (C-5), 124.06 (C-6), 132.11 (C-7), 116.34 (C-8), 120.23 (C-9), 152.05 (C-10).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_3\text{S}\cdot\text{HBr}$: C, 55.37; H, 3.10; N, 10.76. Found: C, 55.12; H, 2.98; N, 10.38.

4-Hydroxy-3-(2-methylamino-thiazol-4-yl)-chromen-2-one (**3b**).

This compound was obtained from the reaction with 1-(methyl)-thiourea as yellow needles (from ethanol) in a yield of 0.52 g (67 %), mp 218-220°, $R_f=0.42$ (silica gel, methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr): 3433, 3381, 3155, 3116 (OH) and (NH), 1698 (C=O), 1630, 1513, 1409, 1340, 1299, 1185, 1092, 960 cm^{-1} ; ^1H nmr (DMSO-d_6): δ 2.98 (s, 3H, CH_3), 7.29-7.84 (m, 4H, 6-H, 7-H, 5-H, 8-H, $^4J_{7,5}=1.63$ Hz, $^4J_{6,8}=1.18$ Hz, $^3J_{8,7}=8.35$ Hz, $^3J_{6,5}=7.89$ Hz, $^3J_{6,7}=7.37$ Hz), 7.38 (s, H, 5'-H), 11.01 (bs, 1H, NH), 16.36 (s, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 159.42, (C-2'), 109.46, (C-5'), 141.67 (C-4'), 156.32 (C-2), 168.39 (C-4), 32.34 (CH_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3\text{S}$: C, 56.92; H, 3.67; N, 10.26. Found: C, 56.62; H, 3.98; N, 10.28.

4-Hydroxy-3-(2-phenylamino-thiazol-4-yl)-chromen-2-one (**3c**).

This compound was obtained from the reaction with 1-(phenyl)-thiourea as yellow needles (from ethanol) in a yield of 0.42 g (70%), mp 224-226°, $R_f=0.64$ (silica gel, methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr): 3483 (NH), 3261 (OH), 3030, 1684, (C=O), 1615, 1533, 1459, 1165, 1072, 966 cm^{-1} ; ^1H nmr (DMSO-d_6): δ 7.37-7.85 (m, 4H, 6-H, 7-H, 5-H, 8-H, $^4J_{7,5}=1.63$ Hz, $^4J_{6,8}=1.17$ Hz, $^3J_{8,7}=8.34$ Hz, $^3J_{6,5}=7.87$ Hz, $^3J_{6,7}=7.35$ Hz) 6.8-7.2 (m, 5H, phenyl), 8.11 (s, 1H, 5'-H), 10.31 (bs, 1H, NH), 12.85 (s, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 159.42 (C-2'), 119.36, (C-5'), 150.37 (C-4'), 156.32 (C-2), 168.78 (C-4).

Anal. Calcd. for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$: C, 64.27; H, 3.61; N, 8.33. Found: C, 63.98; H, 3.78; N, 8.28.

4-hydroxy-3-(2-p-tolylamino-thiazol-4-yl)-chromen-2-one (**3d**).

This compound was obtained from the reaction with 1-(4-methylphenyl)thiourea as yellow needles (from ethanol) in a yield of 0.78 g (63%), mp 208-210°, $R_f=0.58$ (silica gel, methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr) 3287 (OH), 3147 (NH), 3082, 1692 (C=O), 1621, 1591, 1432, 1356, 1106, 1052, 866 cm^{-1} . ^1H nmr (DMSO-d_6): δ 2.23 (s, 3H, CH_3), 7.29-7.82 (m, 4-H, 6-H, 7-H, 5-H, 8-H, $^4J_{7,5}=1.63$ Hz, $^4J_{6,8}=1.15$ Hz, $^3J_{8,7}=8.37$ Hz, $^3J_{6,5}=7.89$ Hz, $^3J_{6,7}=7.34$ Hz), 7.12-7.21 (ABq, 4H, phenyl, $^3J=8.41$ Hz), 8.24 (s, 1H, 5-H), 9.86 (bs, 1H, NH), 14.22 (bs, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 20.67 (CH_3), 153.92 (C-2'), 118.56 (C-5'), 150.67 (C-4'), 145.62 (C-1, phenyl), 129.78 (C-4, phenyl).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$: C, 64.13; H, 4.03; N, 7.99. Found: C, 63.99; H, 4.10; N, 8.13.

4-Hydroxy-3-[2-(4-methoxy-phenylamino)-thiazol-4-yl]-chromen-2-one (**3e**).

This compound was obtained from the reaction with 1-(4-methoxyphenyl)thiourea as pale orange needles (from ethanol) in a yield of 0.964 g (74 %), mp 198-200°, $R_f=0.46$ (silica gel,

methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr): 3476 (NH), 3251 (OH), 3076, 1686 (C=O), 1665, 1563, 1459, 1365, 1002, 846 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.35-7.85 (m, 4H, 6-C, 7-C, 5-C, 8-C, $^4J_{7,5}=1.61$ Hz, $^4J_{6,8}=1.15$ Hz, $^3J_{8,7}=8.31$ Hz, $^3J_{6,5}=7.85$ Hz, $^3J_{6,7}=7.33$ Hz), 6.81-7.05 (ABq, 4H, phenyl, $^3J=8.90$ Hz), 8.17 (s, 1H, 5'-H), 10.09 (bs, 1H, NH), 14.85 (bs, 1H, OH); ^{13}C nmr (DMSO- d_6): δ 154.52 (C-2'), 118.86 (C-5'), 150.27 (C-4'), 153.32 (C-4), 139.78 (C-1).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$: C, 62.28; H, 3.85; N, 7.65. Found: C, 62.56; H, 3.79; N, 7.48.

Reaction of 3-(2-Bromoacetyl)-4-hydroxychromen-2-one (2) with Thioamides.

A mixture of 3-(2-bromoacetyl)-4-hydroxychromen-2-one (2) (1 g, 3.5 mmol) and thioamide (3.5 mmol) in absolute ethanol (90 ml) was heated for 30-45 min under refluxing. After cooling, the precipitate was collected and recrystallized to give 4-hydroxy-3-(thiazol-4-yl)-chromen-2-one (4a-b).

4-Hydroxy-3-(2-methyl-thiazol-4-yl)-chromen-2-one (4a).

This compound was obtained from the reaction with methylthioamide as orange needles (ethanol) in a yield of 0.186 g (72%), mp 182-184°, $R_f=0.32$ (silica gel, methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr) 3378 (OH), 3030, 1697 (C=O), 1615, 1533, 1459, 1390, 1165, 1072, 966 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 2.46 (s, 3H, CH_3), 7.29-7.80 (m, 4H, 6-H, 7-H, 5-H, 8-H, $^4J_{7,5}=1.62$ Hz, $^4J_{6,8}=1.15$ Hz, $^3J_{8,7}=8.37$ Hz, $^3J_{6,5}=7.9$ Hz, $^3J_{6,7}=7.39$ Hz), 8.28 (bs, 1H, 5'-H), 15.36 (bs, 1H, OH); ^{13}C nmr (DMSO- d_6): δ 162.02 (C-2'), 111.96 (C-5'), 144.27 (C-4'), 154.32 (C-2), 167.99 (C-4), 18.38 (CH_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{NO}_3\text{S}$: C, 60.22; H, 3.50; N, 5.40. Found: C, 59.86; H, 3.82; N, 5.28.

4-Hydroxy-3-(2-phenyl-thiazol-4-yl)-chromen-2-one (4b).

This compound was obtained from the reaction with phenylthioamide as orange needles (from ethanol) in a yield of 0.186 g (74%), mp 189-191°, $R_f=0.45$ (silica gel, methyl-ethyl ketone:toluene, 1:9); ir (KBr) 3165 (OH), 3011, 1691 (C=O), 1619, 1532, 1439, 1373, 1163, 1077, 969 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.10-7.82 (m, 9H, phenyl and 6-H, 7-H, 5-H, 8-H), 8.29 (s, 1H, 5'-H), 15.19 (s, 1H, OH); ^{13}C nmr (DMSO- d_6): δ 167.12 (C-2'), 112.96 (C-5'), 144.87 (C-4'), 155.92 (C-2), 168.77 (C-4).

Anal. Calcd. for $\text{C}_{18}\text{H}_{11}\text{NO}_3\text{S}$: C, 67.28; H, 3.45; N, 4.36. Found: C, 66.92; H, 3.81; N, 4.28.

4-Hydroxy-3-(2-mercapto-thiazol-4-yl)-chromen-2-one (5).

A mixture of 3-(2-bromoacetyl)-4-hydroxy-chromen-2-one (2) (0.285 g, 1 mmol) and ammonium dithiocarbamate (0.110 g, 1

mmol) in absolute ethanol (30 ml) was heated for 30 minutes under refluxing. The precipitate was collected and recrystallized from 70% ethanol to afford 4-hydroxy-3-(2-mercapto-thiazol-4-yl)-chromen-2-one (5) as yellow-orange needles, yield 0.39 g (81%), mp 204-206°, $R_f=0.42$ (silica gel, methyl-ethyl ketone:toluene, 1:9, v/v); ir (KBr): 3305 (OH), 3021, 1682 (C=O), 1621, 1533, 1474, 1396, 1166, 1067, 962 cm^{-1} ; ^1H nmr (DMSO): δ 3.46 (s, 1H, SH), 8.23 (s, 1H, 5'-H), 15.23 (s, 1H, OH); ^{13}C nmr (DMSO): δ 153.12 (C-2'), 112.86 (C-5'), 144.37 (C-4'), 156.22 (C-2), 168.77 (C-4).

Anal. Calcd. for $\text{C}_{12}\text{H}_7\text{NO}_3\text{S}_2$: C, 51.97; H, 2.54; N, 5.05. Found: C, 51.55; H, 2.91; N, 5.28.

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