

### 3-(2-QUINOLYL)- AND 3-(5-CARBETHOXYFURYL-2)COUMARINS

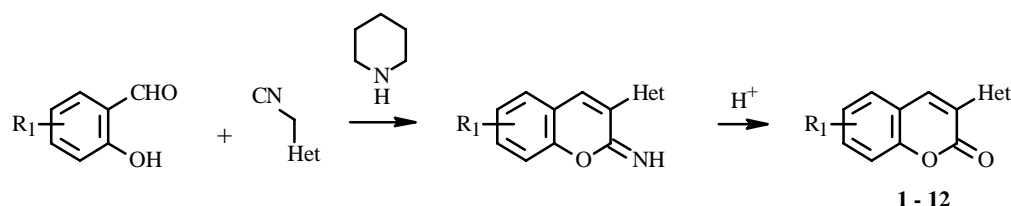
O. V. Shablykina, O. V. Khilya,  
V. V. Ishchenko, and V. P. Khilya

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*3-(2-Quinolyl)- and 3-(5-carbethoxyfuryl-2)coumarins were prepared by reaction of substituted salicylaldehydes and hetarylacetonitriles. Alkylation and acylation of 3-hetaryl-7-hydroxycoumarins were studied.*

**Key words:** 3-(2-quinolyl)coumarins, 3-(5-carbethoxyfuryl-2)coumarins, 7-alkoxy-3-(2-quinolyl)coumarins, 7-alkoxy-3-(5-carbethoxyfuryl-2)coumarins, 7-acyloxy-3-(2-quinolyl)coumarins, 7-acyloxy-3-(5-carbethoxyfuryl-2)coumarins.

The variety of synthetic 3-hetarylcoumarins includes few with furan [1, 2] and quinoline [3] rings. The furan ring is found in many substances of natural origin, as a rule, in the hydrogenated form (furanose form of carbohydrates, alkaloid pilocarpine) and in synthetic biologically active compounds (furacilin antibiotics). Natural derivatives of quinoline, namely the alkaloids of cinchona tree bark quinine and cinchonine, were first used as antimalarials. Therefore, it was interesting to prepare and study coumarins with furan and quinoline as the heterocyclic substituent. Coumarins **1-12** were synthesized by condensation of substituted salicylaldehydes and hetarylacetonitriles with subsequent hydrolysis of the resulting 2-iminocoumarins in acidic medium (Scheme 1) [4]:



**1 - 6:** Het = 2-quinolyl; **1:** R<sub>1</sub> = H; **2:** R<sub>1</sub> = 7-OH; **3:** R<sub>1</sub> = 6-NO<sub>2</sub>; **4:** R<sub>1</sub> = 6-Cl; **5:** R<sub>1</sub> = 6,8-Cl<sub>2</sub>;  
**6:** R<sub>1</sub> = 6-Br; **7 - 12:** Het = 2-(5-carbethoxyfuryl); **7:** R<sub>1</sub> = 7-OH; **8:** R<sub>1</sub> = 8-OH; **9:** R<sub>1</sub> = 7,8-(OH)<sub>2</sub>;  
**10:** R<sub>1</sub> = 6-NO<sub>2</sub>; **11:** R<sub>1</sub> = 6-Cl; **12:** R<sub>1</sub> = 6-Br

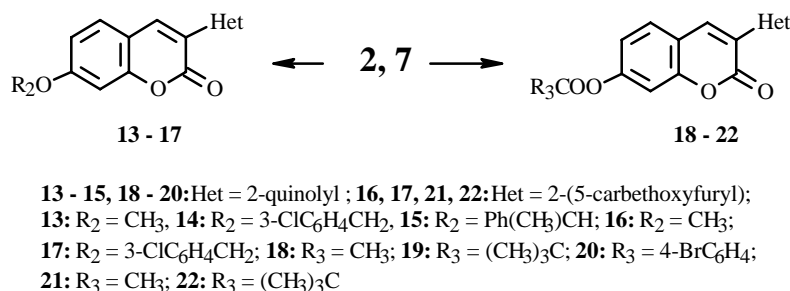
Scheme 1.

The presence of the electron-accepting 5-carbethoxy substituent in the furan ring not only increases the activity of acetonitrile as the methylene component of the condensation but also increases the stability of the furan ring under the reaction conditions.

The structures of the resulting compounds were proved by PMR spectroscopy. Proton chemical shifts are given in the Experimental section.

Scheme 2 shows further modification of the products by alkylation and acylation of the reactive 7-OH in **2** and **7**.

Coumarins **1-22** are primarily high-melting and weakly colored compounds that are soluble in polar organic solvents. Their solutions (except compounds with a nitro group) are intensely fluorescent.



Scheme 2.

The effect of the substituents in the coumarin ring on the electron-density distribution in the heterocyclic substituent is interesting. Protons 3' and 4' of the quinoline ring in **1** and **3-6** appear as two doublets with  $^3J = 8$  Hz. For **2**, these protons are magnetically equivalent and appear as a 2H singlet. With an alkoxyl substituent in the coumarin 7-position (**13-15**), H-3' and H-4' also appear as a singlet or narrow multiplet. However, acylation of the 7-OH in **2** causes these protons in **18-20** to become nonequivalent (two doublets). In **7-12** and in **16** and **17** with a furan substituent, H-3' and H-4' of the furan are nonequivalent, two doublets with  $^3J = 4$  Hz. However, in 7-acyloxycoumarins **21** and **22**, they appear as a 2H singlet.

Thus, condensation of salicylaldehydes and hetarylacetonitriles produced new coumarins with quinoline and furan substituents in the 3-position. 7-O-Alkyl- and 7-O-acyl- derivatives were prepared from 7-hydroxycoumarins.

## EXPERIMENTAL

General comments have been published [5].

### General Method for Synthesizing 3-(2-Quinolyl)coumarins 1-6 and 3-(5-Carbethoxyfuryl-2-)coumarins 7-12.

Substituted salicylaldehyde (0.1 mol) and hetarylacetonitrile (0.1 mol) were dissolved in the minimal volume of ethanol or isopropanol at 60°C and treated with piperidine (0.1 mL). The reaction mixture was held for 1 d at room temperature, treated with H<sub>2</sub>SO<sub>4</sub> (50 mL, 3%), and boiled 2-12 h to hydrolyze the iminocoumarin. After the reaction was finished, the solid coumarin was filtered off and thoroughly washed with water.

Crystallization: **1**, **7**, **8**, ethanol; **9**, aqueous ethanol; **2-6** and **10-12**, DMF.

**3-(2-Quinolyl)coumarin (1).** Yield 82%, C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub>, mp 163-163.5°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.39 (1H, br.t,  $^3J = 8$ , H-6), 7.44 (1H, d,  $^3J = 8$ , H-8), 7.59 (1H, br.t,  $^3J = 8$ , H-6'), 7.65 (1H, br.t,  $^3J = 8$ , H-7), 7.77 (1H, br.t,  $^3J = 8$ , H-7'), 7.90 (1H, dd,  $^3J = 8$ ,  $^4J = 1.5$ , H-5), 7.95 (1H, d,  $^3J = 8$ , H-5'), 8.08 (1H, d,  $^3J = 8$ , H-8'), 8.31 (1H, d,  $^3J = 8.5$ , H-3'), 8.37 (1H, d,  $^3J = 8.5$ , H-4'), 8.91 (1H, s, H-4).

**7-Hydroxy-3-(2-quinolyl)coumarin (2).** Yield 81%, C<sub>18</sub>H<sub>11</sub>NO<sub>3</sub>, mp 267-267.5°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 6.76 (1H, d,  $^4J = 2$ , H-8), 6.83 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.56 (1H, br.t,  $^3J = 8$ , H-6'), 7.69 (1H, d,  $^3J = 8$ , H-5), 7.74 (1H, br.t,  $^4J = 8$ , H-7'), 7.93 (1H, d,  $^3J = 8$ , H-5'), 8.05 (1H, d,  $^3J = 8$ , H-8'), 8.33 (2H, s, H-3', H-4'), 8.85 (1H, s, H-4), 10.66 (1H, br.s, OH-7).

**6-Nitro-3-(2-quinolyl)coumarin (3).** Yield 86%, C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>, mp 245-247°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.59-7.67 (2H, m, H-6', H-8), 7.78 (1H, br.t,  $^3J = 8$ , H-7'), 7.97 (1H, d,  $^3J = 8$ , H-5'), 8.09 (1H, d,  $^3J = 8$ , H-8'), 8.29 (1H, d,  $^3J = 8.5$ , H-3'), 8.39 (1H, d,  $^3J = 8.5$ , H-4'), 8.44 (1H, dd,  $^3J = 9$ ,  $^4J = 1.5$ , H-7), 8.91 (1H, br.s, H-5), 9.07 (1H, s, H-4).

**6-Chloro-3-(2-quinolyl)coumarin (4).** Yield 96%, C<sub>18</sub>H<sub>10</sub>ClNO<sub>2</sub>, mp 199-200°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.45 (1H, d,  $^3J = 8.5$ , H-8), 7.57-7.63 (2H, m, H-7, H-6'), 7.76 (1H, br.t,  $^3J = 8$ , H-7'), 7.95 (1H, d,  $^3J = 8$ , H-5'), 7.98 (1H, d,  $^3J = 2$ , H-5), 8.06 (1H, d,  $^3J = 8$ , H-8'), 8.28 (1H, d,  $^3J = 8.5$ , H-3'), 8.37 (1H, d,  $^3J = 8.5$ , H-4'), 8.86 (1H, s, H-4).

**6,8-Dichloro-3-(2-quinolyl)coumarin (5).** Yield 88%, C<sub>18</sub>H<sub>9</sub>Cl<sub>2</sub>NO<sub>2</sub>, mp 224-225°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.60 (1H, br.t,  $^3J = 8$ , H-6'), 7.74-7.79 (2H, m, H-5, H-7'), 7.97 (1H, d,  $^3J = 8$ , H-5'), 8.00 (1H, d,  $^4J = 2$ , H-7), 8.06 (1H, d,  $^3J = 8$ , H-8'), 8.27 (1H, d,  $^3J = 8.5$ , H-3'), 8.39 (1H, d,  $^3J = 8.5$ , H-4'), 8.87 (1H, s, H-4).

**6-Bromo-3-(2-quinolyl)coumarin (6).** Yield 83%, C<sub>18</sub>H<sub>10</sub>BrNO<sub>2</sub>, mp 225-226°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.41 (1H, d,  $^3J = 8.5$ , H-8), 7.60 (1H, br.t,  $^3J = 8$ , H-6'), 7.72-7.79 (2H, m, H-7, H-7'), 7.95 (1H, d,  $^3J = 8$ , H-5'), 8.07 (1H, d,  $^3J = 8$ , H-8'), 8.12 (1H, d,  $^4J = 2$ , H-5), 8.30 (1H, d,  $^3J = 8.5$ , H-3'), 8.37 (1H, d,  $^3J = 8.5$ , H-4'), 8.89 (1H, s, H-4).

**7-Hydroxy-3-(5-carbethoxyfuryl-2)coumarin (7).** Yield 79%,  $C_{16}H_{12}O_6$ , mp 225-226°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $COOCH_2CH_3$ -5'), 4.33 (2H, q,  $COOCH_2CH_3$ -5'), 6.73 (1H, d,  $J = 2$ , H-8), 6.81 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.20 (1H, d,  $^3J = 4$ , H-3'), 7.28 (1H, d,  $^3J = 4$ , H-4'), 7.70 (1H, d,  $^3J = 8.5$ , H-5), 8.37 (1H, s, H-4), 10.64 (1H, br.s, OH-7).

**8-Hydroxy-3-(5-carbethoxyfuryl-2)coumarin (8).** Yield 76%,  $C_{16}H_{12}O_6$ , mp 213-214°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.39 (3H, t,  $COOCH_2CH_3$ -5'), 4.34 (2H, q,  $COOCH_2CH_3$ -5'), 7.11 (1H, dd,  $^3J = 8.5$ ,  $^4J = 1.5$ , H-7), 7.15 (1H, t,  $^3J = 8.5$ , H-6), 7.28 (1H, dd,  $^3J = 8.5$ ,  $^4J = 1.5$ , H-5), 7.30 (1H, d,  $^3J = 4$ , H-3'), 7.34 (1H, d,  $^3J = 4$ , H-4'), 8.41 (1H, s, H-4), 10.16 (1H, br.s, OH-8).

**7,8-Dihydroxy-3-(5-carbethoxyfuryl-2)coumarin (9).** Yield 69%,  $C_{16}H_{12}O_7$ , mp 238-240°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $COOCH_2CH_3$ -5'), 4.33 (2H, q,  $COOCH_2CH_3$ -5'), 6.83 (1H, d,  $^3J = 8.5$ , H-6), 7.19 (1H, d,  $^3J = 8.5$ , H-5), 7.22 (1H, d,  $^3J = 4$ , H-3'), 7.27 (1H, d,  $^3J = 4$ , H-4'), 8.33 (1H, s, H-4), 9.41 (1H, br.s, OH-8), 10.15 (1H, br.s, OH-7).

**6-Nitro-3-(5-carbethoxyfuryl-2)coumarin (10).** Yield 93%,  $C_{16}H_{11}NO_7$ , mp 225-227°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.39 (3H, t,  $COOCH_2CH_3$ -5'), 4.35 (2H, q,  $COOCH_2CH_3$ -5'), 7.32 (1H, d,  $^3J = 4$ , H-3'), 7.36 (1H, d,  $^3J = 4$ , H-4'), 7.62 (1H, d,  $^3J = 8.5$ , H-8), 8.40 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2.5$ , H-7), 8.71 (1H, s, H-4), 8.98 (1H, d,  $^4J = 2.5$ , H-5).

**6-Chloro-3-(5-carbethoxyfuryl-2)coumarin (11).** Yield 89%,  $C_{16}H_{11}ClO_5$ , mp 152-152.5°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $COOCH_2CH_3$ -5'), 4.34 (2H, q,  $COOCH_2CH_3$ -5'), 7.29 (1H, d,  $^3J = 4$ , H-3'), 7.33 (1H, d,  $^3J = 4$ , H-4'), 7.40 (1H, d,  $^3J = 8.5$ , H-8), 7.57 (1H, br.d,  $^3J = 8.5$ , H-7), 8.01 (1H, br.s, H-5), 8.46 (1H, s, H-4).

**6-Bromo-3-(5-carbethoxyfuryl-2)coumarin (12).** Yield 91%,  $C_{16}H_{11}BrO_5$ , mp 172-173°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $COOCH_2CH_3$ -5'), 4.34 (2H, q,  $COOCH_2CH_3$ -5'), 7.30 (1H, d,  $^3J = 4$ , H-3'), 7.34 (1H, d,  $^3J = 4$ , H-4'), 7.37 (1H, d,  $^3J = 8.5$ , H-8), 7.71 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2.5$ , H-7), 8.17 (1H, d,  $^3J = 2.5$ , H-5), 8.49 (1H, s, H-4).

**General Method for Synthesizing 7-Alkoxy-3-(2-quinolyl)coumarins 13-15 and 7-Alkoxy-3-(5-carbethoxyfuryl-2)coumarins 16 and 17.** A mixture of **2** or **7** (2.5 mmol), alkylchloride (3.5 mmol; for **13** and **16**, dimethylsulfate), and freshly calcined potash (1 g) was boiled in absolute acetone (20 mL) with stirring for 8-10 h. Solvent was evaporated. The solid was worked up with water. The solid was filtered off.

Crystallization: DMF:isopropanol.

**7-Methoxy-3-(2-quinolyl)coumarin (13).** Yield 63%,  $C_{19}H_{13}NO_3$ , mp 198-199°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 3.92 (3H, s, 7-OMe), 6.96 (1H, dd,  $^3J = 8$ ,  $^4J = 1.5$ , H-6), 7.02 (1H, d,  $^4J = 1.5$ , H-8), 7.56 (1H, br.t,  $^3J = 8$ , H-6'), 7.74 (1H, br.t,  $^3J = 8$ , H-7'), 7.80 (1H, d,  $^3J = 8$ , H-5), 7.93 (1H, d,  $^3J = 8$ , H-5'), 8.05 (1H, d,  $^3J = 8$ , H-8'), 8.33 (2H, s, H-3', H-4'), 8.90 (1H, s, H-4).

**7-(3-Chlorobenzoyloxy)-3-(2-quinolyl)coumarin (14).** Yield 65%,  $C_{25}H_{16}ClNO_3$ , mp 202-203°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 5.26 (2H, s, 7-OCH<sub>2</sub>), 7.05 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.14 (1H, d,  $^4J = 2$ , H-8), 7.33-7.43 (3H, m, 3-ClC<sub>6</sub>H<sub>4</sub>), 7.53 (1H, br.s, 3-ClC<sub>6</sub>H<sub>4</sub>), 7.60 (1H, br.t,  $^3J = 8$ , H-6'), 7.76 (1H, br.t,  $^3J = 8$ , H-7'), 7.83 (1H, d,  $^3J = 8.5$ , H-5), 7.95 (1H, d,  $^3J = 8$ , H-5'), 8.06 (1H, d,  $^3J = 8$ , H-8'), 8.31-8.38 (2H, m, H-3', H-4'), 8.90 (1H, s, H-4).

**7-( $\alpha$ -Methylbenzyloxy)-3-(2-quinolyl)coumarin (15).** Yield 71%,  $C_{26}H_{19}NO_3$ , mp 186-187°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.64 [3H, d,  $^3J = 6.5$ , 7-OCH(CH<sub>3</sub>)Ph], 5.62 [1H, q,  $^3J = 6.5$ , 7-OCH(CH<sub>3</sub>)Ph], 6.90 (1H, d,  $^4J = 2$ , H-8), 6.93 (1H, dd,  $^3J = 8$ ,  $^4J = 2$ , H-6), 7.25 (1H, br.t,  $^3J = 8$ , Ph), 7.34 (2H, br.t,  $^3J = 8$ , Ph), 7.43 (2H, br.d,  $^3J = 8$ , Ph), 7.54 (1H, br.t,  $^3J = 8$ , H-6'), 7.69-7.74 (2H, m, H-5, H-7'), 7.90 (1H, d,  $^3J = 8$ , H-5'), 8.03 (1H, d,  $^3J = 8$ , H-8'), 8.29 (2H, s, H-3', H-4'), 8.82 (1H, s, H-4).

**7-Methoxy-3-(5-carbethoxyfuryl-2)coumarin (16).** Yield 76%,  $C_{17}H_{14}O_6$ , mp 160-162°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $COOCH_2CH_3$ -5'), 3.90 (3H, s, 7-OMe), 4.32 (2H, q,  $COOCH_2CH_3$ -5'), 6.94 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 6.98 (1H, d,  $^4J = 2$ , H-8), 7.23 (1H, d,  $^3J = 4$ , H-3'), 7.27 (1H, d,  $^3J = 4$ , H-4'), 7.80 (1H, d,  $^3J = 8.5$ , H-5), 8.42 (1H, s, H-4).

**7-(3-Chlorobenzoyloxy)-3-(5-carbethoxyfuryl-2)coumarin (17).** Yield 73%,  $C_{23}H_{17}ClO_6$ , mp 177-178°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $\text{COOCH}_2\text{CH}_3$ -5'), 4.33 (2H, q,  $\text{COOCH}_2\text{CH}_3$ -5'), 5.23 (2H, s, 7-OCH<sub>2</sub>), 7.03 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.10 (1H, d,  $^4J = 2$ , H-8), 7.23 (1H, d,  $^3J = 4$ , H-3'), 7.28 (1H, d,  $^3J = 4$ , H-4'), 7.35 (1H, m, 3-ClC<sub>6</sub>H<sub>4</sub>), 7.41 (2H, m, 3-ClC<sub>6</sub>H<sub>4</sub>), 7.51 (1H, m, 3-ClC<sub>6</sub>H<sub>4</sub>), 7.85 (1H, d,  $^3J = 8.5$ , H-5), 8.44 (1H, s, H-4).

**General Method for Synthesizing 7-Acyloxy-3-(2-quinolyl)coumarins 18-20 and 7-Acyloxy-3-(5-carbethoxyfuryl-2)coumarins 21 and 22.** A solution of **2** or **7** (2.5 mmol) in pyridine (5 mL) was treated with acid chloride (or anhydride) (5 mmol) and heated at ~80°C for 10-15 min. The reaction mixture was left for 1 d at room temperature and poured onto ice. The solid 7-acyloxy coumarin was filtered off.

Crystallization: DMF:isopropanol.

**7-Acetyloxy-3-(2-quinolyl)coumarin (18).** Yield 90%, C<sub>20</sub>H<sub>13</sub>NO<sub>4</sub>, mp 227-228°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 2.34 (3H, s, MeCOO-7), 7.17 (1H, dd,  $^3J = 8$ ,  $^4J = 1.5$ , H-6), 7.28 (1H, d,  $^4J = 1.5$ , H-8), 7.60 (1H, br.t,  $^3J = 8$ , H-6'), 7.77 (1H, br.t,  $^3J = 8$ , H-7'), 7.95-7.98 (2H, m, H-5, H-5'), 8.08 (1H, d,  $^3J = 8$ , H-8'), 8.30 (1H, d,  $^3J = 8$ , H-3'), 8.38 (1H, d,  $^3J = 8$ , H-4'), 8.93 (1H, s, H-4).

**7-Pivalyloxy-3-(2-quinolyl)coumarin (19).** Yield 56%, C<sub>23</sub>H<sub>19</sub>NO<sub>4</sub>, mp 185-186°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.14 (9H, s, Me<sub>3</sub>CCOO-7), 7.13 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.23 (1H, d,  $^4J = 2$ , H-8), 7.59 (1H, br.t,  $^3J = 8$ , H-6'), 7.76 (1H, br.t,  $^3J = 8$ , H-7'), 7.94-7.98 (2H, m, H-5, H-5'), 8.07 (1H, d,  $^3J = 8$ , H-8'), 8.31 (1H, d,  $^3J = 8$ , H-3'), 8.37 (1H, d,  $^3J = 8$ , H-4'), 8.94 (1H, s, H-4).

**7-(4-Bromobenzoyl)-3-(2-quinolyl)coumarin (20).** Yield 85%, C<sub>22</sub>H<sub>14</sub>BrO<sub>4</sub>, mp 266°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 7.42 (1H, br.d,  $^3J = 8.5$ , H-6), 7.59 (1H, br.s, H-8), 7.65 (1H, br.t,  $^3J = 8$ , H-6'), 7.81-7.86 [3H, m, H-7', H-3'', H-5'' (4-BrC<sub>6</sub>H<sub>4</sub>)], 8.03 (1H, d,  $^3J = 8.5$ , H-5), 8.08-8.13 [4H, m, H-5', H-8', H-2'', H-6'' (4-BrC<sub>6</sub>H<sub>4</sub>)], 8.28 (1H, d,  $^3J = 8$ , H-3'), 8.47 (1H, d,  $^3J = 8$ , H-4'), 8.95 (1H, s, H-4).

**7-Acetyloxy-3-(5-carbethoxyfuryl-2)coumarin (21).** Yield 92%, C<sub>18</sub>H<sub>14</sub>O<sub>7</sub>, mp 198-199°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.38 (3H, t,  $\text{COOCH}_2\text{CH}_3$ -5'), 2.33 (3H, s, MeCOO-7), 4.35 (2H, q,  $\text{COOCH}_2\text{CH}_3$ -5'), 7.15 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.25 (1H, d,  $^4J = 2$ , H-8), 7.32 (2H, s, H-3', H-4'), 7.99 (1H, d,  $^3J = 8.5$ , H-5), 8.52 (1H, s, H-4).

**7-Pivalyloxy-3-(5-carbethoxyfuryl-2)coumarin (22).** Yield 59%, C<sub>21</sub>H<sub>20</sub>O<sub>7</sub>, mp 172-173°C.

PMR spectrum ( $\delta$ , ppm, J/Hz): 1.14 (9H, s, Me<sub>3</sub>CCOO-7), 1.39 (3H, t,  $\text{COOCH}_2\text{CH}_3$ -5'), 4.35 (2H, q,  $\text{COOCH}_2\text{CH}_3$ -5'), 7.12 (1H, dd,  $^3J = 8.5$ ,  $^4J = 2$ , H-6), 7.20 (1H, d,  $^4J = 2$ , H-8), 7.31 (2H, s, H-3', H-4'), 7.98 (1H, d,  $^3J = 8.5$ , H-5), 8.50 (1H, s, H-4).

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