Chemistry of Natural Compounds, Vol. 45, No. 2, 2009

MODIFIED COUMARINS. 30. SYNTHESIS OF 6-HETEROARYLCOUMARINS

I. V. Nagorichna,[1] A. A. Tkachuk,[1] M. M. Garazd,[1*] Ya. L. Garazd,[2] and V. P. Khilya[2]

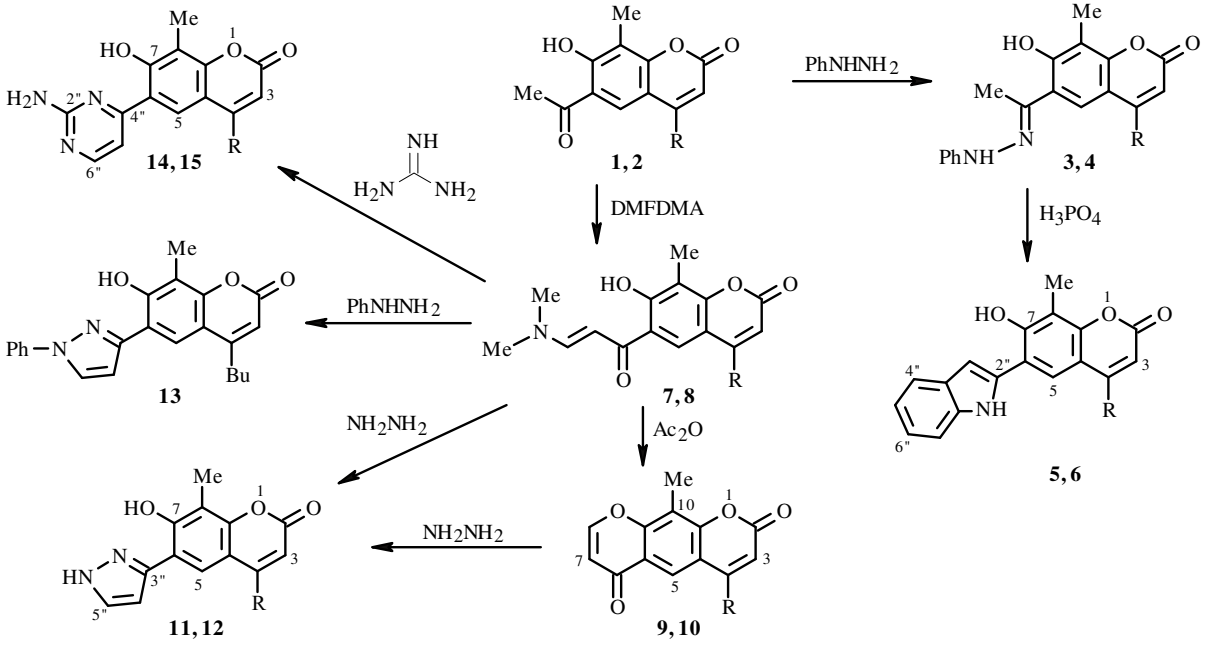
UDC 547.814.5

Heteroarylcoumarins containing 2-indole, 3-pyrazole, and 4-pyrimidine substituents in the 6-position of the coumarin ring were synthesized.

Key words: coumarins, heteroarylcoumarins, enaminones, heterocyclization.

The benzopyran-2-one moiety is found in the molecular structure of many important natural secondary metabolites [1] and compounds with high pharmacological activity [2]. Modification of the benzopyran-2-one moiety by judicious introduction of a heterocyclic ring into the molecule has recently become an active topic in coumarin chemistry [3, 4]. This research is interesting to the theory of organic synthesis and the targeted synthesis of new biologically active compounds based on the coumarin core.

In most instances the hetaryl substituent is introduced at the 3- or 4-position of the coumarin ring judging from syntheses of coumarins containing heterocyclic rings in the benzene ring of the benzopyran-2-one [4]. Herein we report the synthesis of coumarins with indole, pyrazole, and pyrimidine rings in the 6-position of the benzopyran-2-one moiety.



1, 3, 5, 7, 9, 11, 14: R = $CH_2CH_2CH_3$; **2, 4, 6, 8, 10, 12, 15:** R = $CH_2CH_2CH_2CH_3$

1) Institute of Bioorganic and Petroleum Chemistry, National Academy of Sciences of Ukraine, 02094, Ukraine, Kiev, ul. Murmanskaya, 1, e-mail: gmm@i.com.ua; 2) Taras Shevchenko Kiev National University, 01033, Ukraine, Kiev, ul. Vladimirskaya, 64. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 145-148, March-April, 2009. Original article submitted January 14, 2008.

 0009-3130/09/4502-0164

The 6-acetyl-7-hydroxy-8-methyl-4-alkylchromen-2-ones (**1**) and (**2**) required for further transformations were prepared by Fries rearrangement of the corresponding 7-acetoxycoumarins [5]. Condensation of 7-acetoxycoumarins **1** and **2** with *N*-phenylhydrazine produced phenylhydrazones **3** and **4**, intramolecular heterocyclization of which under Fisher synthesis conditions using polyphosphoric acid at 120°C [6] formed 7-hydroxy-6-(indol-2-yl)-8-methyl-4-alkylchromen-2-ones **5** and **6**. NMR spectra of **5** and **6** showed resonances characteristic of the coumarin system and the formed indole ring.

We used enaminones **7** and **8**, which were prepared by condensation of the dimethylacetal of *N*,*N*-dimethylformamide (DMFDMA) with 6-acetylcoumarins **1** and **2**, as convenient starting materials for the synthesis of coumarins with pyrazole and pyrimidine substituents [7, 8].

Brief heating of enaminones **7** and **8** in acetic anhydride led to annelation of the pyran-4-one ring [9, 10] in the coumarin system to form 10-methyl-4-alkylpyrano[3,2-*g*]chromen-2,6-diones **9** and **10**. The PMR spectra of these compounds showed resonances for the coumarin system and two doublets with SSCC J = 6.0 Hz at 6.38 and 8.34 ppm that were characteristic of an annelated pyran-4-one ring [11]. ^{13}C NMR spectra of **9** and **10** had resonances at 176 and 159 ppm that were characteristic of carbonyl groups of the chromone and coumarin ring, respectively.

Hydrazine is known to react with compounds with a chromone ring to open the pyranone ring and close a pyrazole ring [12]. Brief heating of alcoholic solutions of **9** and **10** with an excess of hydrazine led to recyclization of the pyrano [3,2-*g*]chromen-2,6-dione system into 7-hydroxy-8-methyl-4-alkyl-6-(pyrazol-3-yl)chromen-2-ones (**11** and **12**). In contrast with starting pyranocoumarins **9** and **10**, coumarins **11** and **12** form with an alcoholic solution of $FeCl_3$ a characteristic blue-green chelate complex due to the phenolic hydroxyl and the pyrazole nitrogen. PMR spectra of **11** and **12** showed resonances for the coumarin system and two doublets with SSCC J = 2.4 Hz at 7.12 and 8.00 ppm that were characteristic of H-4 and H-5 of the formed pyrazole ring and two broad singlets for the NH- and OH-protons at 12.20 and 13.30 ppm, respectively. The presence of a hydroxyl proton resonance at weak field (13.30 ppm) was consistent with the presence of an intramolecular interaction between the hydroxyl and the pyrazole nitrogen.

6-(Pyrazol-3-yl)chromen-2-ones **11** and **12** were also prepared by treatment of an alcoholic solution of enaminones **7** and **8** with an excess of hydrazone [7, 8]. Enaminone **8** was reacted analogously with phenylhydrazine to form 6-(1-phenylpyrazol-3-yl)chromen-2-one **13**.

Reaction of enaminones **7** and **8** with guanidinium hydrochloride in pyridine resulted in the formation of the pyrimidine ring [7] and led to the formation of 6-(2-aminopyrimidin-4-yl)chromen-2-ones **14** and **15**. Coumarins **14** and **15** and an alcoholic solution of $FeCl_3$ formed a characteristic blue-green chelate complex due to the phenolic hydroxyl and the pyrimidine nitrogen. PMR spectra of **14** and **15** showed resonances for the coumarin system and two doublets with SSCC J = 5.6 Hz at 7.40 and 8.40 ppm that were characteristic of H-5 and H-6 of the pyrimidine ring. A characteristic feature of the PMR spectra of **14** and **15** was the separate absorption of the NH_2 and OH protons. A 2H broad singlet for the amino group appeared at 7.10-7.20 ppm. The resonance of the hydroxy proton at weak field (15.20 ppm) was consistent with a strong intramolecular H-bond between the hydroxyl and the pyrimidine nitrogen.

EXPERIMENTAL

The course of reactions and the purity of products were monitored by TLC on Merck 60 F254 plates with elution by $CHCl_3$:CH_3OH (9:1 and 95:5). Melting points were determined on a Kofler block. NMR spectra were measured on Varian VXR-300 and Varian Mercury 400 spectrometers at 300 and 400 MHz, respectively, relative to TMS (internal standard). Elemental analyses of all compounds agreed with those calculated.

The syntheses of 6-acetyl-7-hydroxycoumarins **1** and **2** have been reported [5].

Phenylhydrazones 3 and 4. A solution of **1** or **2** (10 mmol) and phenylhydrazine (0.25 mL, 25 mmol) in ethanol (10 mL) was refluxed for 1 h and cooled. The resulting precipitate was filtered off and crystallized from propanol-2.

7-Hydroxy-8-methyl-6-(*N*-phenylethanehydrazonoyl)-4-propylchromen-2-one (3). Yield 95%, mp 273-274°C, $C_{21}H_{22}N_2O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.04 (3H, t, J = 7.2, CH_3-3′), 1.73 (2H, m, CH_2-2′), 2.25 (3H, s, CH_3-8), 2.47 (3H, s, CH_3CN-6), 2.81 (2H, t, J = 7.2, CH_2-1′), 6.06 (1H, s, H-3), 6.85 (1H, m, H-4″), 7.07 (2H, d, J = 7.8, H-3″, H-5″), 7.28 (2H, t, J = 7.8, H-2″, H-6″), 7.62 (1H, s, H-5), 9.55 (1H, s, NH), 13.99 (1H, s, OH).

4-Butyl-7-hydroxy-8-methyl-6-(*N*-phenylethanehydrazonoyl)chromen-2-one (4). Yield 90%, mp 262-263°C, $C_{22}H_{24}N_2O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.98 (3H, t, J = 7.2, CH_3-4′), 1.44 (2H, m, CH_2-3′), 1.65 (2H, m, CH_2-2′), 2.25 (3H, s, CH_3-8), 2.45 (3H, s, CH_3CN-6), 2.81 (2H, t, J = 7.2, CH_2-1′), 6.04 (1H, s, H-3), 6.85 (1H, m, H-4″), 7.06 (2H, d, J = 7.8, H-3″, H-5″), 7.28 (2H, t, J = 7.8, H-2″, H-6″), 7.63 (1H, s, H-5), 9.57 (1H, s, NH), 14.00 (1H, s, OH).

6-(Indol-2-yl)coumarins 5 and 6. A mixture of phenylhydrazone **3** or **4** (5 mmol) and polyphosphoric acid (20 mL) was held at 120•C for 1 h, cooled, poured into icewater (300 mL), and neutralized with $NaHCO_3$ solution (10%). The resulting precipitate was filtered off and crystallized from propanol-2.

7-Hydroxy-6-(indol-2-yl)-8-methyl-4-propylchromen-2-one (5). Yield 62%, mp 243-244°C, $C_{21}H_{19}NO_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.02 (3H, t, J = 7.2, CH_3-3′), 1.73 (2H, m, CH_3-2′), 2.33 (3H, s, CH_3-8), 2.87 (2H, t, J = 7.2, CH_2-1′), 6.18 (1H, s, H-3), 7.02 (1H, t, J = 7.6, H-6″), 7.04 (1H, s, H-3″), 7.11 (1H, t, J = 7.6, H-5″), 7.47 (1H, d, J = 7.6, H-7″), 7.56 (1H, d, J = 7.6, H-4″), 7.92 (1H, s, H-5), 9.81 (1H, s, NH), 11.35 (1H, s, OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 160.96 (C-2), 157.76 (C-4), 156.15 (C-8a), 152.40 (C-7), 134.79 (C-7″), 129.05 (C-2″), 122.03 (C-4a), 121.72 (C-5″), 120.63 (C-6), 119.76 (C-3″), 118.63 (C-4″), 113.45 (C-5), 112.72 (C-8), 110.62 (C-6″), 110.58 (C-3), 102.9 (C-1″), 33.34 (C-1′), 21.84 (C-2′), 14.41 (C-3′), 8.75 (CH_3-8).

4-Butyl-7-hydroxy-6-(indol-2-yl)-8-methylchromen-2-one (6). Yield 71%, mp 221-223°C, $C_{22}H_{21}NO_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.95 (3H, t, J = 7.2, CH_3-4′), 1.45 (2H, m, CH_2-3′), 1.66 (2H, m, CH_2-2′), 2.32 (3H, s, CH_3-8), 2.89 (2H, t, J = CH_2-1′), 6.16 (1H, s, H-3), 7.00 (1H, t, J = 7.6, H-6″), 7.02 (1H, s, H-3″), 7.11 (1H, t, J = 7.6, H-5″), 7.47 (1H, d, J = 7.6, H-7″), 7.56 (1H, d, J = 7.6, H-4″), 7.91 (1H, s, H-5), 9.75 (1H, s, NH), 11.38 (1H, s, OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 161.12 (C-2), 158.05 (C-4), 157.65 (C-8a), 152.57 (C-7), 135.42 (C-7″), 129.03 (C-2″), 121.84 (C-4a), 121.61 (C-5″), 120.50 (C-6), 119.71 (C-3″), 118.51 (C-4″), 113.42 (C-5), 111.87 (C-8), 109.92 (C-6″), 109.58 (C-3), 102.11 (C-1″), 31.18 (C-1′), 30.80 (C-2′), 22.60 (C-3′), 14.48 (C-4′), 9.74 (CH_3-8).

Enaminones 7 and 8. A mixture of coumarin **1** or **2** (10 mmol) and DMFDMA (2 mL, 15 mmol) in anhydrous toluene (20 mL) was refluxed for 24 h (end of reaction determined using TLC). The resulting precipitate was filtered off and crystallized from propanol-2.

6-[3-(Dimethylamino)prop-2-enoyl]-7-hydroxy-8-methyl-4-propylchromen-2-one (7). Yield 84%, mp 197-198°C, $C_{18}H_{21}NO_4$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.99 (3H, t, J = 7.2, CH_3-3′), 1.67 (2H, m, CH_2-2′), 2.14 (3H, s, CH_3-8), 2.85 (2H, t, J = 7.2, CH_2-1′), 3.08 (3H, s, NCH_3), 3.25 (3H, s, NCH_3), 6.01 (1H, d, J = 11.6, H-2″), 6.12 (1H, s, H-3), 7.99 (1H, d, J = 11.6, H-3″), 8.01 (1H, s, H-5), 12.15 (1H, s, OH).

4-Butyl-6-[3-(dimethylamino)prop-2-enoyl]-7-hydroxy-8-methylchromen-2-one (8). Yield 63%, mp 185-186°C, $C_{19}H_{23}NO_4$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.96 (3H, t, J = 7.2, CH_3-4′), 1.42 (2H, m, CH_2-3′), 1.60 (2H, m, CH_2-2′), 2.15 (3H, s, CH_3-8), 2.87 (2H, t, J = 7.2, CH_2-1′), 3.06 (3H, s, NCH_3), 3.25 (3H, s, NCH_3), 5.99 (1H, d, J = 11.6, H-2″), 6.14 (1H, s, H-3), 7.99 (1H, d, J = 11.6, H-3″), 8.01 (1H, s, H-5), 11.90 (1H, s, OH).

10-Methyl-4-alkylylpyrano[3,2-*g*]chromen-2,6-diones 9 and 10. A solution of enaminone **7** or **8** (3 mmol) in freshly distilled acetic anhydride (5 mL) was refluxed for 5 h (end of reaction determined using TLC) and cooled. The resulting precipitate was filtered off and crystallized from propanol-2.

10-Methyl-4-propylpyrano[3,2-*g*]chromen-2,6-dione (9). Yield 68%, mp 181-182°C, $C_{16}H_{14}O_4$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.03 (3H, t, J = 7.2, CH_3-3′), 1.73 (2H, m, CH_2-2′), 2.44 (3H, s, CH_3-10), 2.85 (2H, t, J = 7.2, CH_2-1′), 6.38 (1H, d, J = 6.0, H-7), 6.40 (1H, s, H-3), 8.21 (1H, s, H-5), 8.34 (1H, d, J = 6.0, H-8).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 176.47 (C-6), 159.52 (C-2), 157.98 (C-10a), 156.57 (C-4), 155.83 (C-8), 154.24 (C-9a), 120.83 (C-5a), 119.73 (C-5), 117.14 (C-4a), 115.1 (C-10), 113.99 (C-7), 112.51 (C-3), 33.37 (C-1′), 21.39 (C-2′), 14.30 (C-3′), 8.75 (CH_3-8).

4-Butyl-10-methylpyrano[3,2-*g*]chromen-2,6-dione (10). Yield 84%, mp 156-157°C, $C_{17}H_{16}O_4$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.95 (3H, t, J = 7.2, CH_3-4′), 1.44 (2H, m, CH_2-3′), 1.63 (2H, m, CH_2-2′), 2.42 (3H, s, CH_3-10), 2.86 (2H, t, J = 7.2, CH_2-1′), 6.41 (1H, d, J = 6.0, H-7), 6.42 (1H, s, H-3), 8.18 (1H, s, H-5), 8.40 (1H, d, J = 6.0, H-7).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 176.37 (C-6), 159.44 (C-2), 157.9 (C-10a), 156.71 (C-4), 155.75 (C-8), 154.32 (C-9a), 120.83 (C-5a), 119.73 (C-5), 117.05 (C-4a), 115.03 (C-10), 113.85 (C-7), 112.48 (C-3), 31.15 (C-1′), 30.12 (C-2′), 22.57 (C-3′), 14.36 (C-4′), 8.69 (CH_3-8).

6-(Pyrazol-3-yl)chromen-2-ones 11 and 12. Method A. A solution of dione **9** or **10** (2 mmol) in ethanol (5 mL) was treated with hydrazine monohydrate (0.49 mL, 10 mmol), refluxed for 1 h (end of reaction determined using TLC), and cooled. The resulting precipitate was filtered off and dried.

Method B. A solution of enaminone **7** or **8** (2 mmol) in ethanol (5 mL) was treated with hydrazine monohydrate (0.30 mL, 6 mmol), refluxed for 1-2 h (end of reaction determined using TLC), and cooled. The resulting precipitate was filtered off and dried.

7-Hydroxy-8-methyl-4-propyl-6-(pyrazol-3-yl)chromen-2-one (11). Yield 88%, mp 194-195°C, $C_{16}H_{16}N_2O_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.00 (3H, t, J = 7.2, CH_3-3′), 1.68 (2H, m, CH_2-2′), 2.24 (3H, s, CH_3-8), 2.83 (2H, t, J = 7.2, CH_2-1′), 6.12 (1H, s, H-3), 7.12 (1H, d, J = 2.4, H-4″), 7.93 (1H, s, H-5), 8.00 (1H, d, J = 2.4, H-5″), 12.20 (1H, br.s, NH), 13.30 (1H, br.s, OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 160.92 (C-2), 157.59 (C-4), 157.29 (C-8a), 152.43 (C-7), 150.43 (C-3″), 130.9 (C-5″), 120.30 (C-4a), 114.29 (C-6), 112.27 (C-5), 112.01 (C-8), 110.17 (C-3), 102.72 (C-4″), 33.21 (C-1′), 21.78 (C-2′), 14.31 (C-3′), 8.74 (CH_3-8).

4-Butyl-7-hydroxy-8-methyl-6-(pyrazol-3-yl)chromen-2-one (12). Yield 84%, mp 181-182°C, $C_{17}H_{18}N_2O_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.94 (3H, t, J = 7.2, CH_3-4′), 1.42 (2H, m, CH_2-3′), 1.60 (2H, m, CH_2-2′), 2.23 (3H, s, CH_3-8), 2.83 (2H, t, J = 7.2, CH_2-1′), 6.11 (1H, s, H-3), 7.08 (1H, d, J = 2.4, H-4″), 7.91 (1H, s, H-5), 8.00 (1H, d, J = 2.4, H-5″), 12.25 (1H, br.s, NH), 13.20 (1H, br.s, OH).

4-Butyl-7-hydroxy-8-methyl-6-(1-phenylpyrazol-3-yl)chromen-2-one (13). A solution of enaminone **8** (0.66 g, 2 mmol) in ethanol (5 mL) was treated with phenylhydrazine (0.59 mL, 6 mmol), refluxed for 2 h (end of reaction determined using TLC), and cooled. The resulting precipitate was filtered and dried. Yield 64%, mp 194-195°C, $C_{23}H_{22}N_2O_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.96 (3H, t, J = 7.2, CH_3-4′), 1.44 (2H, m, CH_2-3′), 1.64 (2H, m, CH_2-2′), 2.29 (3H, s, CH_3-8), 2.90 (2H, t, J = 7.2, CH_2-1′), 6.18 (1H, s, H-3), 7.39 (1H, t, J = 7.6, H-4‴), 7.44 (1H, d, J = 2.8, H-4″), 7.58 (2H, t, J = 7.6, H-3‴, H-5‴), 7.91 (2H, d, J = 7.6, H-2‴, H-6‴), 8.05 (1H, s, H-5), 8.77 (1H, d, J = 2.4, H-5″), 11.65 (1H, s, OH).

6-(2-Aminopyrimidin-4-yl)chromen-2-ones 14 and 15. A mixture of enaminone **7** or **8** (2 mmol) and guanidinium hydrochloride (0.29 g, 3 mmol) in pyridine (5 mL) was refluxed for 8-10 h (end of reaction determined using TLC), poured into water (100 mL), and acidified with acetic acid. The resulting precipitate was filtered off and crystallized from propanol-2.

6-(2-Aminopyrimidin-4-yl)-7-hydroxy-8-methyl-4-propylchromen-2-one (14). Yield 82%, mp 203-204°C, $C_{17}H_{17}N_3O_3$.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.01 (3H, t, J = 7.2, CH_3-3′), 1.67 (2H, m, CH_2-2′), 2.21 (3H, s, CH_3-8), 2.83 (2H, t, J = 7.2, CH_2-1′), 6.11 (1H, s, H-3), 7.16 (2H, br.s, NH_2), 7.40 (1H, d, J = 5.6, H-5″), 8.08 (1H, s, H-5), 8.45 (1H, d, J = 5.6, H-6″), 15.15 (1H, br.s, OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 161.36 (C-2), 160.52 (C-2″, C-4″), 157.43 (C-4, C-8a), 154.42 (C-7), 152.03 (C-6″), 110.03 (C-3), 121.95 (C-4a), 113.84 (C-6), 113.04 (C-5), 111.52 (C-8), 104.65 (C-5″), 33.02 (C-1′), 21.50 (C-2′), 14.34 (C-3′), 8.50 (CH_3-8).

6-(2-Aminopyrimidin-4-yl)-4-butyl-7-hydroxy-8-methylchromen-2-one (15). Yield 87%, mp 196-197°C, $C_{18}H_{19}N_3O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.95 (3H, t, J = 7.2, CH_3-4′), 1.42 (2H, m, CH_2-3′), 1.63 (2H, m, CH_2-2′), 2.22 (3H, s, CH_3-8), 2.86 (2H, t, J = 7.2, CH_2-1′), 6.11 (1H, s, H-3), 7.14 (2H, br.s, NH_2), 7.38 (1H, d, J = 5.6, H-5″), 8.08 (1H, s, H-5), 8.41 (1H, d, J = 5.6, H-6″), 15.19 (1H, br.s, OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 161.47 (C-2), 160.69 (C-2″), 159.87 (C-4″), 157.88 (C-4, C-8a), 154.46 (C-7), 152.03 (C-6″), 122.19 (C-4a), 113.84 (C-6), 113.14 (C-5), 110.19 (C-3), 104.75 (C-5″), 111.64 (C-8), 30.9 (C-1″), 30.58 (C-2′), 22.26 (C-3′), 14.43 (C-4′), 8.57 (CH_3-8).

ACKNOWLEDGMENT

We thank OAO Eximed (Kiev, Ukraine) for help in performing the work.

REFERENCES

1. R. D. H. Murray, *Progress in the Chemistry of Organic Natural Products. The Naturally Occurring Coumarins*, Springer, Vienna, New York (2002).
2. R. O'Kennedy and R. D. Thornes, *Coumarins - Biology, Applications and Mode of Action*, John Wiley & Sons Ltd., Chichester (1997).
3. S. M. Kovalenko, I. E. Bylov, K. M. Sytnik, and V. P. Chernykh, *Molecules*, 1146 (2000).
4. V. P. Khilya, O. V. Shablykina, and V. V. Ishchenko, *Selected Methods of Heterocycle Synthesis and Modification* [in Russian], Vol. 2, V. G. Kartsev, ed., IBS PRESS, Moscow (2003), p. 518.
5. I. V. Nagorichna, M. M. Garazd, Ya. L. Garazd, and V. P. Khilya, *Khim. Prir. Soedin.*, 135 (2009).
6. A. H. Abdel-Rahman, A. M. Khalil, S. I. El-Desoky, and E. M. Keshk, *Chem. Pap.*, **53**, 323 (1999).
7. K. M. Al-Zaydi, *Molecules*, 541 (2003).
8. E. M. Keshk, *Heteroat. Chem.*, **15**, 85 (2004).
9. B. Fohlisch, *Chem. Ber.*, **104**, 348 (1971).
10. H. Yoshimura, M. Nagai, S. Hibi, K. Kikuchi, S. Abe, T. Hida, S. Higashi, I. Hishinuma, and T. Yamanaka, *J. Med. Chem.*, **38**, 3163 (1996).
11. M. E. Perel′son, Yu. N. Sheinker, and A. A. Savina, *Spectra and Structure of Coumarins, Chromones, and Xanthones* [in Russian], Meditsina, Moscow (1975).
12. V. V. Arkhipov, M. M. Garazd, M. N. Smirnov, and V. P. Khilya, *Khim. Geterotsikl. Soedin.*, 218 (2004).