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SYNTHESIS OF NEW CONDENSED COUMARIN DERIVATIVES

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Abstract. *Reactions of 4-chloro-2-oxo-2H-chromene-3-carbonitrile (1) with 4-methyl-pyridin-2-ylamine (2) and 6-methoxy-benzothiazol-2-ylamine (3) in acetonitrile containing a catalytic amount of triethylamine gave the new coumarin derivatives 7-imino-10-methyl-7H-5-oxa-7a,12-diaza-benzo[a]anthracen-6-one (4) and 7-imino-10-methoxy-7H-5-oxa-12-thia-7a,13-diaza-indeno[1,2-b]phenanthren-6-one (5) in 52 and 39% yields, respectively. The novel compounds were subjected to acid hydrolysis giving the corresponding oxoderivatives 10-methyl-5-oxa-7a,12-diaza-benzo[a]anthracene-6,7-dione (6) and 10-methoxy-5-oxa-12-thia-7a,13-diaza-indeno[1,2-b]phenanthrene-6,7-dione (7) in 64 and 58% yields, respectively. The structural assignments of the synthesized compounds were based on elemental analyses, IR and proton NMR spectra.*

Key words: *synthesis, hydrolysis, structural determination*

INTRODUCTION

The synthesis of coumarin (2-oxo-2*H*-chromene) derivatives has attracted considerable attention of organic and medicinal chemists as these are widely used as fragrances, pharmaceuticals and agrochemicals [1]. Having in mind the wide variety of their usage, we thought it worthwhile to synthesize new coumarin derivatives.

EXPERIMENT

General methods. Melting points were measured with a Kofler hot-plate apparatus and are uncorrected. The elemental analyses were performed on a Carlo Erba 1106 micro-analyzer. The IR measurements were carried out with a Perkin-Elmer 137 spectrometer using KBr pellets. The NMR spectra were recorded on a Varian A-60 spectrometer, using DMSO-d_6 as a solvent. Chemical shifts are expressed in δ (ppm) using TMS (tetramethylsilane) as an internal standard.

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Starting materials. 4-Hydroxy-2-oxo-2H-chromene-3-carbonitrile was prepared following the method of Anschutz [2]. 4-Chloro-2-oxo-2H-chromene-3-carbonitrile **(1)**, a starting compound, was prepared from 4-hydroxy-2-oxo-2H-chromene-3-carbonitrile according to the method of Chechi et al. [3], modified by Kaljaj et al. [4] in order to obtain higher yields (from 35-40% to 96%) and shorter reaction time (from 7 hours to less then 1 hour). The preparation was carried out in the following manner: 1.85 ml of absolute dimethyl-formamide (DMF) was cooled to 10 ^{o}C (ice bath) and, while stirring, 4 g of $POCl_3$ was added drop-wise. The reaction mixture was stirred in the ice bath for 15 minutes, then the ice bath was removed and the reaction was kept at room temperature for additional 15 minutes. Then, the solution of 4-hydroxy-2-oxo-2H-chromene-3-carbonitrile (4.67 g) in DMF (12.5 ml) was added drop-wise. After 15 minutes of stirring, the reaction was stopped by adding cold water (15 ml). The precipitate solid was filtered and washed with a saturated sodium-bicarbonate solution, and then with water. Recrystalization from glacial acetic acid yielded yellow crystals of **1** (4.8 g) in 96% yield, mp 199-200 ^{o}C. Finally, all other chemicals were commercially available and used as received, except that the solvents were purified by distillation.

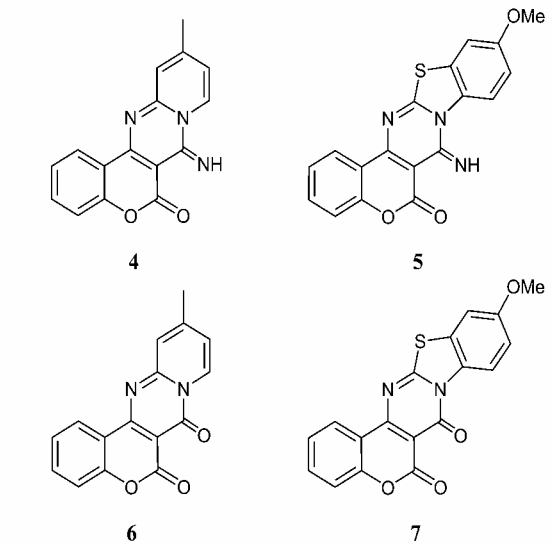


Fig. 1. Structures of the new synthesized coumarin derivates

General procedure for the synthesis of coumarin derivatives 4-5. A solution of **1** (2.0 g, 10 mmol) and the appropriate heteroarylamine (4-methyl-pyridin-2-ylamine (**2**), 6-methoxy-benzothiazol-2-ylamine (**3**), 10 mmol) in acetonitrile (30 ml) in the presence of catalytic amounts of triethylamine (2 ml) was refluxed for 1-2 hours. After cooling, the precipitate solid was filtered off and washed with ethanol. Recrystalization from DMF yielded compound **4-5**, respectively. The purity of the synthesized compounds was checked by TLC.

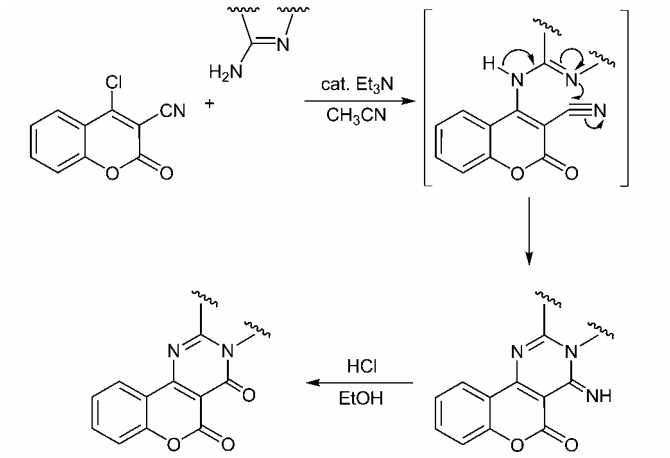
7-Imino-10-methyl-7*H*-5-oxa-7a,12-diaza-benzo[*a*]anthracen-6-one (4). Yellow crystals, yield 1.6 g (52%), mp 293-294 ^{o}C; IR ν (KBr, cm^{-1}): 3290 (N-H), 3100 (Ar-H), 2910 (C-H from CH_3), 1680 (α-pyrone C=O), 1625 (C=N), 1610 (C=C), 765; ^{1}H NMR (DMSO-d_6): δ =

9.90 (brs, 1H, N-H), 8.20-7.15 (m, 7H, arom.), 2.90 (s, 3H, CH_3) ppm; Anal. calcd. for $C_{16}H_{11}N_3O_2$ (277.28): C, 69.31; H, 4.00; N, 15.15. Found: C, 69.18; H, 4.25; N, 15.32.

7-Imino-10-methoxy-7*H*-5-oxa-12-thia-7a,13-diaza-indeno[1,2-*b*]phenanthren-6-one (5). Yellow crystals, yield 1.48 g (39%), mp 278-280 °C; IR ν (KBr, cm^{-1}): 3300 (N-H), 3090 (Ar-H), 2940 (C-H from CH_3), 1705 (α-pyrone C=O), 1640 (C=N), 1600 (C=C), 760; ^1H NMR (DMSO-d_6): δ = 9.85 (brs, 1H, N-H), 8.30-7.10 (m, 7H, arom.), 3.85 (s, 3H, CH_3O) ppm; Anal. calcd. for $C_{18}H_{11}N_3O_3S$ (349.36): C, 61.88; H, 3.17; N, 12.03; S, 9.18. Found: C, 62.15; H, 2.98; N, 11.80; S, 9.05.

General procedure for the preparation of oxoderivatives 6-7. Each of compounds **4-5** (1 g) was heated under reflux for 1 hour with 15% hydrochloric acid (20 ml) in ethanol (50 ml). After cooling, a precipitate was filtered and washed with a saturated sodium bicarbonate solution, and then with water. Recristalization from ethanol yielded compounds **6-7**, respectively.

10-Methyl-5-oxa-7a,12-diaza-benzo[*a*]anthracene-6,7-dione (6). Yield 0.64 g (64%), mp 312-314 °C; IR ν (KBr, cm^{-1}): 3085 (Ar-H), 2915 (C-H from CH_3), 1760 (α-pyrimidone C=O), 1685 (α-pyrone C=O), 1615 (C=N), 1600 (C=C), 750; ^1H NMR (DMSO-d_6): δ = 8.25-7.20 (m, 7H, arom.), 3.00 (s, 3H, CH_3) ppm; Anal. calcd. for $C_{16}H_{10}N_2O_3$ (278.26): C, 69.06; H, 3.62; N, 10.07. Found: C, 68.84; H, 3.82; N, 10.35.



Scheme 1. The general synthetic approach to the new coumarin derivates

10-Methoxy-5-oxa-12-thia-7a,13-diaza-indeno[1,2-*b*]phenanthrene-6,7-dione (7). Yield 0.58 g (58%), mp 302-304 °C; IR ν (KBr, cm^{-1}): 3100 (Ar-H), 2950 (C-H from CH_3), 1765 (α-pyrimidone C=O), 1710 (α-pyrone C=O), 1640 (C=N), 1610 (C=C), 765; ^1H NMR (DMSO-d_6): δ = 8.20-7.10 (m, 7H, arom.), 3.85 (s, 3H, CH_3O) ppm; Anal. calcd. for $C_{18}H_{10}N_2O_4S$ (350.35): C, 61.71; H, 2.88; N, 8.00; S, 9.15. Found: C, 62.02; H, 2.95; N, 7.68; S, 9.32.

RESULTS AND DISCUSSION

New coumarin derivatives **4-5** (Figure 1) were prepared by reaction of 4-chloro-2-oxo-2*H*-chromene-3-carbonitrile **(1)** with 4-methyl-pyridin-2-ylamine (**2**) and 6-methoxy-benzothiazol-2-ylamine (**3**), respectively, catalyzed by triethylamine in acetonitrile according to the procedure of Chechi et al [3] (Scheme 1). The compounds **4-5** were subjected to acid hydrolysis and afforded the corresponding oxoderivatives **6-7** (Scheme 1). The structures were assigned by comparison of their spectral data (IR and ^{1}H NMR) to those published in the literature for related systems [4–8].

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SINTEZA NOVIH KONDENZOVANIH DERIVATA KUMARINA

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Reakcijama 4-hlor-2-okso-2H-hromen-3-karbonitrila (1) sa 4-metil-piridin-2-ilaminom (2) i 6-metoksi-benzotiazol-2-ilaminom (3) u acetonitrilu u prisustvu trietilamina kao katalizatora dobijeni su novi derivati kumarina 7-imino-10-metil-7H-5-oksa-7a,12-diaza-benzo[a]antracen-6-on (4) i 7-imino-10-metoksi-7H-5-oksa-12-tia-7a,13-diaza-indeno[1,2-b]fenantren-6-on (5) sa prinosima od 52%, odnosno 39%. Hidrolizom dobijenih jedinjenja u kiseloj sredini dobijeni su odgovarajući dioni 6-7 sa prinosima od 64%, odnosno 58%. Strukture sintetizovanih jedinjenja određene su na osnovu podataka dobijenih elementnom analizom, IC i protonskom NMR spektoskopijom.