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КРАТКИЕ СООБЩЕНИЯ

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CO-CRYSTAL STRUCTURE OF MIXED MOLECULES OF METHYL 2-(3-CHLORO-4-METHYL-2-OXO-2H-CHROMEN-7-YLOXY)ACETATE AND 2-(2-AMINOPHENYL)BENZOTHIAZOLE

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A co-crystal is obtained in a methanolic solution from methyl 2-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yloxy)acetate and 2-(2-aminophenyl)benzothiazole. In the crystal these molecules are connected via usual N—H…O and weak C—H…O H-bonds. The co-crystals are very stable.

Keywords: 2-(2-aminophenyl)benzothiazole, co-crystal, coumarins, methanol, single crystal X-ray.

Drug resistance has become a growing problem in the treatment of infectious diseases caused by bacteria and fungi [1, 2]. Coumarin and its derivatives represent one of the most active classes of compounds possessing a wide spectrum of biological activity [3—7]. Structure activity relationships of coumarin derivatives have revealed that the presence of substituted amino derivatives is an essential feature of their pharmacological action. Based on these findings, we tried to describe the synthesis of some compounds featuring different heterocyclic rings fused onto the coumarin moiety with the aim of obtaining more potent pharmacologically active compounds, but the reaction did not occur.

Experimental. The chemicals used during the synthesis were supplied by Sigma-Aldrich. Purity of the compounds was checked on thin layer chromatography (TLC) plates (Silica gel G) in benzene: ethyl acetate : methanol (40:30:30, v/v/v) and toluene : acetone (75:25, v/v) solvent systems. The spots were located under UV light 254 nm and 365 nm.

General procedure for the synthesis of the co-crystal. A mixture of 0.05 mol of 2-(2-aminophenyl)benzothiazole and 0.05 mol of methyl 2-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yloxy)acetate in methanol was refluxed for 2 h; a suitable co-crystal was obtained by evaporation of the methanol solution.

Crystal structure determination. Diffraction data were collected on a Bruker APEX CCD area-detector diffractometer at 298(2) K on a crystal with dimensions 0.50×0.33×0.26 mm (MoK_α radiation, wavelength 0.71073 Å). Empirical formula $C_{26}H_{21}ClN_2O_5S$; formula weight 508.96, monoclinic, space group $P2_1/n$, unit cell dimensions $a = 12.611(2)$ Å, $b = 7.3544(13)$ Å, $c = 25.980(5)$ Å, $\beta = 99.031(4)°$, $V = 2379.7(7)$ Å^3, $Z = 4$. Calculated density = 1.421 g/cm^3. Absorption coefficient = 0.290 mm^{-1}. $F(000) = 1056$. θ range for data collection 1.59° to 25.50°. Limiting indices $-15 \le h \le 15$, $-8 \le k \le 8$, $-31 \le l \le 23$. Reflections collected / unique 13480 / 4416 [R(int) = 0.0263]. Com-

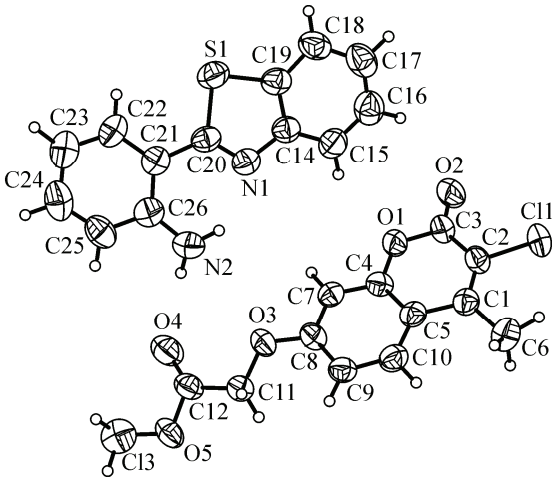

Fig. 1. Crystal structure of the co-crystal

pleteness to θ = 25.50° 99.8 %. Max. and min. transmission 0.9285 and 0.8687. Refinement method: full-matrix least-squares on F^2. Data / restraints / parameters 4416 / 0 / 321. Goodness-of-fit on F^2 1.033. *R* indices (all data) $R_1 = 0.0679$, $wR_2 = 0.1435$. Largest diff. peak and hole 0.524 e/Å^3 and –0.411 e/Å^3.

Results and discussion. From the crystal structure (Fig. 1) it was found that there were two molecules in the crystal structure; the first was methyl 2-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yloxy)acetate and the second 2-(2-aminophenyl)benzothiazole). As shown in Fig. 1, there are hydrogen bonds between methyl 2-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yloxy)acetate and 2-(2-aminophenyl) benzothiazole: N(2)—H…O(4) (H…O distance 2.22(3) Å, N—H…O angle 175(3)°) and weak C(15)—H…O(2) (H…O 2.51 Å, C—H…O 146°).

2-(2-aminophenyl)benzothiazole. The benzothiazole group is not coplanar with the aryl ring; this is attributed to a steric interaction of the aryl group and the amino group with benzothiazole nitrogen. In addition, the C(20)—C(21) bond length is 1.461 Å and the C(22)—C(21)—C(20) bond angle is 119.7° and C(26)—C(21)—C(20) is 121.4°. Moreover, the C(26)—C(21)—C(20)—N(1) torsion angle is 12.7°.

2-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yloxy)acetate (coumarin derivative). From Fig. 1 it is clear that the coumarin molecule is flatter, but there is a steric interaction of the extension of the acetyl group at O(3). The bond lengths of O(3)—C(8) is 1.364 Å and O(3)—C(11) is 1.414 Å, and the bond angles for O(3)—C(8)—C(7) is 114.9°, O(3)—C(8)—C(9) 125.0°, and C(8)—O(3)—C(11) 117.8(2)°. Moreover, the C(8)—O(3)—C(11)—C(12) torsion angle is –178.4°, C(11)—O(3)—C(8)—C(7) is 175.6°, and O(3)—C(11)—C(12)—O(4) is 16.3°.

Conclusions. In this study, the coumarin derivative has been unsuccessfully synthesized. The structure of a stale shiny light brown crystal was determined by X-ray single crystallography and the hydrogen bonding N—H…O and C—H…O was found between the molecules of methyl 2-(2-oxo-2H-chromen-7-yloxy)acetate and 2-(2-aminophenyl)benzothiazole). The bond lengths and bond angles are very close to the corresponding ones found in the Cambridge structural database (ethyl (4-methyl-7-coumarinyloxy)acetate [8], 2-(o-hydroxyphenyl)-1,3-benzothiazol [9] for example).

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