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Synthesis and Biological Study of O–β–*D*–Glucosides of 7–Hydroxy–3–(Disubstituted Imidazol–2–yl)–4*H*–chromen–4–ones

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A series of 7-O-β-D-glucopyranosyloxy-3-(disubstituted imidazol-2-yl)-4H-chromen-4-ones ***5*** *was synthesized. The 7-hydroxy-3-formyl-4H-chromen-4-one* ***1*** *reacted with various 1,2-dicarbonyl compounds* ***2*** *in the presence of ammonium acetate to furnish 7-hydroxy-3-(4,5-disubstitutedimidazol-2-yl)-4H-chromen-4-ones* ***3****, which on glucosylation with α-acetobromoglucose affords 2,3,4,6-tetra-O-acetyl-7-O-β-D-glucopyranosyloxy-3-(4,5-disubstituted imidazol-2-yl)-4H-chromen-4-ones* ***4****. 7-O-β-D-Glucopyranosyloxy-3-(4,5-disubstituted imidazol-2-yl)-4H-chromen-4-ones* ***5*** *were prepared by deacetylation with anhydrous zinc acetate in absolute methanol. Elemental analysis, IR, [1]H NMR, [13]C NMR, EI-MS spectral data were obtained to determine the structure of the newly synthesized compounds.*

Keywords: Chromone, imidazole, acetobromoglucose, glucosylation, glucosides.

Синтез и биологические исследования O–β–D–гликозидов 7–гидрокси–4*H*–хромен–4–онов с 4′,5′–дизамещенными 3–имидазол–2′–ильными фрагментами

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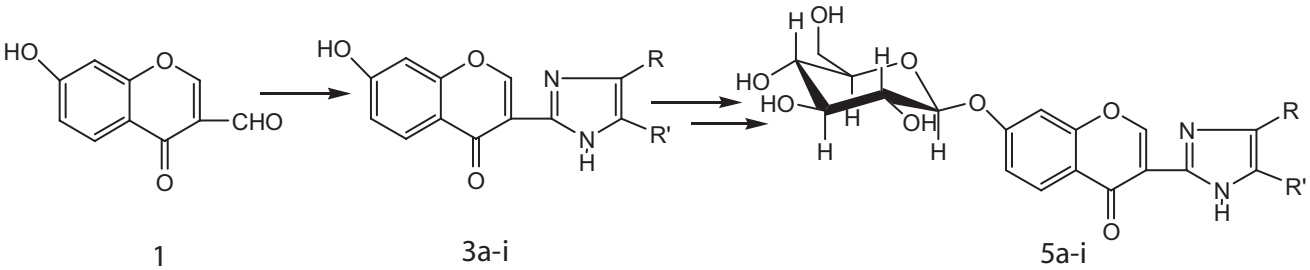
Была синтезирована серия O-β-D-глюкопиранозилкоси-7-гидрокси-4H-хромен-4-онов с 4',5'-дизамещенными 3-имидазол-2'-ильными фрагментами ***5****. 7-Гидрокси-3-формил-4H-хромен-4-он* ***1*** *взаимодействовал с 1,2-дикарбонил замещенными соединениями* ***2*** *в присутствии ацетата аммония с образованием 7-гидрокси-4H-хромен-4-онов с 4',5'-дизамещенными 3-имидазол-2'-ильными фрагментами* ***4****. O-β-D-глюкопиранозилкоси-7-гидрокси-4H-хромен-4-оны с 4',5'-дизамещенными 3-имидазол-2'-ильными фрагментами* ***5*** *были получены деацилированием с безводным ацетатом цинка в абсолютном метаноле. Новые соединения были охарактеризованы с помощью элементного анализа, ИК, [1]H и [13]C ЯМР спектроскопии и масс-спектрометрии (EI-MS).*

Ключевые слова: Хромоны. имидазол, ацетобромоглюкоза, глюкозилирование, гликозиды.

Introduction

Carbohydrates are being considered as extremely useful stereo chemical building blocks for complex organic synthesis.[1] Apart from being an energy source in leaving systems, carbohydrates increasingly are being recognized as playing important roles in a variety of biological processes, such as signaling, cell-cell communications, molecular and cellular targeting.[2] *O-β-D*-Glucosides possess higher degree of biological activities such as cell growth regulation, cell differentiation, immunological response, antitumour, antiparasitic, antifungal activities.[3-11] Several therapeutically interesting biological activities of certain flavonoids have been reported including anticancer,[12-17] anti-HIV,[18-20] and antioxidant[21-23] properties. Similarly imidazoles show antimalerial, antituberculosis, antifungal, anticonvulsant, antiprotozoal, anticancer, antihypertensive, anorectic, hypoglysacemic activities.[24] Considering the above facts and also in continuation of our studies[25] on chromone based heterocycles promoted to prepare several new organic compounds containing chromone, imidazole and glucose moieties. Herein we report the synthesis of new substituted flavonoids 7-hydroxy-3-(imidazol-2-yl)-chromones **3**. These compounds were glucosylated with α-acetobromoglucose yielding 7-*O-β-D*-glucopyranosyloxy-3-(imidazol-2-yl)-chromones **5**.



Experimental

All melting points (mp) measured in open capillary tube were uncorrected. FT-IR spectra were recorded on Perkin-Elmer spectrum Rx-I spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker II-400 NMR spectrophotometer (^{1}H, 400 MHz and ^{13}C, 100 MHz), using TMS as an internal standard in DMSO and $CDCl_3$. Chemical shifts are reported (δ) relative to TMS. Mass spectra were determined on Hitachi Perkin-Elmer RMU 6D mass spectrometer. Elemental analysis for C, H, and N were determined using the Perkin-Elmer 2400 CHN rapid analyzer. Chemicals were obtained from Merck and Fluka and used without further purification. Various 1,2-dicarbonyl compounds were prepared using methods described in literature.[27]

General procedure for the synthesis of compounds ***3a-i.*** A mixture of 7-hydroxy-3-formyl chromone **1** (5 mmol), 1,2-dicarbonyl compounds **2a-i** (5 mmol), ammonium acetate (10 mmol) and glacial acetic acid (50 ml) was refluxed for 2-3 h (monitored by TLC). It was poured on to cold water (200 ml). The solid obtained was filtered, washed with water and crystallized from solvents.

7-Hydroxy-3-(imidazol-2-yl)-chromone ***3a.*** Yield 81 %, mp 290 °C (ethanol). IR (KBr) ν cm^{-1}: 3451 (OH), 2958 (N-H), 1616 (C=O), 1455 (C=N), 1150 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.9 (s, 1′-H, N-H), 7.26 (s, 2-H, CH), 7.05 (d, 2′-H, 3′-H) (CH), 6.40-7.49 (m, 3H, Ar-H), 5.12 (s, 1H, -OH). ^{13}C NMR (DMSO-d_6) δ_C ppm: 174.9 (s, C-4, C=O), 163.9 (s, C-7), 159.8 (s, C-2), 159.0 (s, C-9), 135.9 (s, C-5′), 131.9 (s, C-5), 128.0 (s, C-2′,C-3′), 118.2 (s, C-3), 115.8 (s, C-10), 111.0 (s, C-6), 104.6 (s, C-8). EI-MS *m/z* (%): 229 (M$^+$, 100), 136 (18), 91 (30). Anal. Calcd for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28. Found: C, 63.10; H, 3.51; N, 12.21(%).

7-Hydroxy-3-(4,5-dimethylimidazol-2-yl)-chromone ***3b.*** Yield 76 %, mp 295 °C (chloroform + dioxane). IR (KBr) ν cm^{-1}: 3412 (OH), 2989 (N-H), 1609 (C=O), 1452 (C=N), 1166 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 13.1 (s, 1′-H, N-H), 7.52 (s, 2-H, CH), 6.45-7.50 (m, 3H, Ar-H), 4.99 (s, 1H, -OH), 2.31(s, 2′-H, CH_3), 2.20 (s, 3′-H, CH_3); ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (s, C-4, C=O), 164.5 (s, C-7), 158.9 (s, C-2), 157.8 (s, C-9), 135.7 (s, C-5′), 132.1 (s, C-2′, C-3′), 131.4 (s, C-5), 119.0 (s, C-3), 116.8 (s, C-10), 110.1 (s, C-6), 105.5 (s, C-8), 12.2 (s, CH_3 of C-2′, C-3′). EI-MS *m/z* (%): 257 (M$^+$, 100), 136 (15), 91 (19). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.58; H, 4.72; N, 10.89(%).

7-Hydroxy-3-(4-phenylimidazol-2-yl)-chromone ***3c.*** Yield 78 %, mp 282 °C (ethanol). IR (KBr) ν cm^{-1}: 3400 (OH), 2990 (N-H), 1622 (C=O), 1455 (C=N), 1171 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.7 (s, 1′-H, N-H), 7.56 (s, 2-H, CH), 7.05 (s, 2′-H, CH), 6.41-7.50 (m, 8H, Ar-H), 5.02 (s, 1H, -OH). ^{13}C NMR (DMSO-d_6) δ_C ppm: 174.8 (s, C-4, C=O), 165.1 (s, C-7), 160.0 (s, C-2), 157.5 (s, C-9), 140.1 (s, C-3′), 135.5 (s, C-5′), 132.0 (s, C-5), 125-133.5 (aromatic 6C-atom), 121.0 (s, C-2′), 117.6 (s, C-3), 115.9 (s, C-10), 110.1 (s, C-6), 104.8 (s, C-8). EI-MS *m/z* (%): 305 (M$^+$, 100), 136 (10), 91 (21). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.05; H, 3.97; N, 9.21. Found: C, 71.01; H, 3.93; N, 9.21(%).

7-Hydroxy-3-(4,5-diphenylimidazol-2-yl)-chromone ***3d.*** Yield 90 %, mp 220 °C (chloroform + dioxane). IR (KBr) ν cm^{-1}: 3412 (OH), 2992 (N-H), 1631 (C=O), 1456 (C=N), 1160 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.9 (s, 1′-H, N-H), 7.57 (s, 2-H, CH), 6.43-7.50 (m, 13H, Ar-H), 4.94 (s, 1H, -OH). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.2 (s, C-4, C=O), 164.9 (s, C-7), 159.4 (s, C-2), 157.9 (s, C-9), 135.6 (s, C-5′), 133.1 (s, C-5), 129.0 (s, C-2′, C-3′), 127-133 (aromatic 12C-atom), 117.9 (s, C-3), 117.0 (s, C-10), 109.8 (s, C-6), 106.1 (s, C-8). EI-MS *m/z* (%): 380 (M$^+$, 100), 136 (15), 91 (34). Anal. Calcd for $C_{24}H_{16}N_2O_3$: C, 75.78; H, 4.24; N, 7.36. Found: C, 75.75; H, 4.21; N, 7.35(%).

7-Hydroxy-3-[4-phenyl,5-(p-methoxyphenyl)imidazol-2-yl]-chromone ***3e.*** Yield 89 %, mp 284 °C (chloroform + dioxane). IR (KBr) ν cm^{-1}: 3447 (OH), 2994 (N-H), 1620 (C=O), 1457 (C=N), 1154 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.6 (s, 1′-H, N-H), 7.52 (s, 2-H, CH), 6.38-7.49 (m, 12H, Ar-H), 4.93 (s, 1H, -OH), 3.69 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (s, C-4, C=O), 165.2 (s, C-7), 159.0 (s, C-9), 158.9 (s, C-2), 136.1 (s, C-5′), 131.6 (s, C-5), 128.7 (s, C-2′, C-3′), 119.2 (s, C-3), 117.1 (s, C-10), 115-135 (aromatic 12C-atom), 109.8 (s, C-6), 106.1 (s, C-8), 54.8 (s, C-atom of OCH_3). EI-MS *m/z* (%): 411 (M$^+$, 100), 136 (17), 91 (10). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 73.16; H, 4.42; N, 6.83. Found: C, 73.11; H, 4.39; N, 6.80(%).

7-Hydroxy-3-[4,5-di(o-chlorophenyl)imidazol-2-yl]-chromone ***3f.*** Yield 78 %, mp 231 °C (ethanol), IR (KBr) ν cm^{-1}: 3443 (OH), 2999 (N-H), 1624 (C=O), 1452 (C=N), 1166 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.9 (s, 1′-H, N-H), 7.52 (s, 2-H, CH),

6.41-7.45 (m, 11H, Ar-H), 4.96 (s, 1H, -OH). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (s, C-4, C=O), 164.7 (s, C-7), 159.9 (s, C-2), 159.1 (s, C-9), 136.7 (s, C-5′), 132.0 (s, C-5), 129.9 (s, C-2′, C-3′), 125.0-135.1 (aromatic 12C-atom), 118.1 (s, C-3), 117.2 (s, C-10), 109.9 (s, C-6), 104.6 (s, C-8). EI-MS *m/z* (%): 450 (M^+, 100), 136 (25), 91 (26). Anal. Calcd for $C_{24}H_{16}N_2O_3$: C, 64.16; H, 3.14; N, 6.24. Found: C, 64.12; H, 3.11; N, 6.22(%).

7-Hydroxy-3-[4,5-di(p-chlorophenyl)imidazol-2-yl]-chromone ***3g.*** Yield 83 %, mp 280 °C (ethanol). IR (KBr) ν cm^{-1}: 3449 (OH), 2994 (N-H), 1629 (C=O), 1465 (C=N), 1054 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.2 (s, 1′-H, N-H), 7.43 (s, 2-H, CH), 6.35-7.40 (m, 11H, Ar-H), 4.90 (s, 1H, -OH). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.9 (s, C-4, C=O), 164.1 (s, C-7), 160.1 (s, C-2), 159.6 (s, C-9), 137.0 (s, C-5′), 132.7 (s, C-5), 130.1 (s, C-2′, C-3′), 124.6-135.5 (aromatic 12C-atom), 118.6 (s, C-3), 117.8 (s, C-10), 109.1 (s, C-6), 104.9 (s, C-8). EI-MS *m/z* (%): 450 (M^+, 100), 136 (29), 91 (36). Anal. Calcd for $C_{24}H_{16}N_2O_3$: C, 64.16; H, 3.14; N, 6.24. Found: C, 64.10; H, 3.04; N, 6.16(%).

7-Hydroxy-3-[4,5-di(p-N,N-dimethylaminophenyl)imidazol-2-yl]-chromone ***3h***. Yield 73 %, mp 278 °C (chloroform + dioxane). IR (KBr) ν cm^{-1}: 3433 (OH), 2989 (N-H), 1639 (C=O), 1443 (C=N), 1123 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.8 (s, 1′-H, N-H), 7.23 (s, 2-H, CH), 6.51-7.49 (m, 11H, Ar-H), 4.96 (s, 1H, -OH), 2.88 (s, 6H, N(CH$_3$)$_2$), 2.79 (s, 6H, N(CH$_3$)$_2$). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.2 (s, C-4, C=O), 164.5 (s, C-7), 160.7 (s, C-2), 160.1 (s, C-9), 137.5 (s, C-5′), 132.1 (s, C-5), 130.7 (s, C-2′, C-3′), 124.0-136.1 (aromatic 12C-atom), 118.2 (s, C-3), 117.1 (s, C-10), 109.8 (s, C-6), 105.2 (s, C-8), 40.1 (s, N(CH$_3$)$_2$), 40.7 (s, N(CH$_3$)$_2$). Anal. Calcd for $C_{28}H_{26}N_4O_3$: C, 72.09; H, 5.02; N, 12.01. Found: C, 72.01; H, 4.96; N, 11.92(%).

7-Hydroxy-3-[4,5-di(p-methylphenyl)imidazol-2-yl]-chromone ***3i.*** Yield 82 %, mp 290 °C (chloroform + dioxane). IR (KBr) ν cm^{-1}: 3441 (OH), 2988 (N-H), 1652 (C=O), 1439 (C=N), 1099 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.6 (s, 1′-H, N-H), 7.36 (s, 2-H, CH), 6.29-7.49 (m, 11H, Ar-H), 4.92 (s, 1H, -OH), 2.29 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$); ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.3 (s, C-4, C=O), 164.0 (s, C-7), 160.4 (s, C-2), 159.1 (s, C-9), 137.6 (s, C-5′), 132.2 (s, C-5), 130.4 (s, C-2′, C-3′), 119.7-135.9 (aromatic 12C-atom), 118.2 (s, C-3), 117.1 (s, C-10), 109.8 (s, C-6), 104.1 (s, C-8), 24.0 (s, C-atom of CH$_3$), 23.7 (s, C-atom of CH$_3$). Anal. Calcd for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.36; H, 4.85; N, 6.77(%).

General procedure for the synthesis of compounds ***4a-i***. In a 250 ml round-bottomed flask, anhydrous K_2CO_3 (6.3 mmol) was added to the mixture of dry DMF (9 ml) and acetone (6 ml), then 7-hydroxy-3-(4,5-disubstituted imidazol-2-yl)-chromones **3a-i** (0.30 mmol), DTMAB (10 mg) and α-acetobromoglucose (0.60 mmol) were added under stirring, the reaction mixture was refluxed for 5-6 h (monitored by TLC). Then acetone was removed under vacuum, water (20 ml) was added to the flask. The mixture was extracted with ethyl acetate (5×10 ml), the organic layer was washed by 20 ml water and brine, dried over anhydrous $MgSO_4$, then removed the solvent to give the residue which was purified by silica gel flash chromatography (ethyl acetate: petroleum ether 1:2 v/v) to give a brown coloured semisolid.

*7-(2,3,4,6-Tetra-o-acetyl-o-*β*-d-glucopyranosyloxy)-3-(imidazol-2-yl)-chromone* ***4a.*** Yield 86 %, $[\alpha]_D^{25}$ = - 3.1 (*c* 0.1, CH$_3$OH). IR (KBr) ν cm^{-1}: 2954 (N-H), 2854 (glucosidic-CH), 1761 (C=O of *O*-acetyl gps of glycone moiety), 1722 (C=O), 1646 (C=N), 1052 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.5 (s, 1′-H, N-H), 7.46 (s, 2-H, CH), 7.15 (d, 2′-H, 3′-H) (CH), 6.44-7.43 (m, 3H, Ar-H), 4.87-5.00 (m, 3H, 2″, 3″, 4″-H), 4.76 (d, 1H, 1″-H, anomeric proton), 4.39 (dd, 1H, 5″-H), 3.86-4.24 (m, 2H, 6″-H), 2.01, 1.95, 1.99, 2.05 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 174.9 (C-4, C=O), 171.0 (C-atoms of acetyl C=O), 164.2 (C-7), 159.1 (C-2), 158.1 (C-9), 135.9 (C-5′), 130.9 (C-5), 128.0 (C-2′, C-3′), 117.6 (C-3), 116.2 (C-10), 110.1 (C-6), 103.4 (C-8), 101.9 (C-1″, anomeric C-atom), 74.9 (C-5″), 72.8 (C-2″), 71.5 (C-4″), 71.1 (C-3″), 66.1 (C-6″), 21.8 (C-atom, CH$_3$ of acetyl group). EI-MS *m/z* (%): 559 (M^+, 17), 228 (100), 136 (12), 91 (25). Anal. Calcd for $C_{26}H_{28}O_{12}N_2$: C, 55.91; H, 4.69; N, 5.02. Found: C, 55.89; H, 4.66; N, 5.00(%).

*7-(2,3,4,6-Tetra-o-acetyl-o-*β*-d-glucopyranosyloxy)-3-(4,5-dimethylimidazol-2-yl)-chromone* ***4b.*** Yield 76 %, $[\alpha]_D^{25}$ = - 5.1 (*c* 0.1, CH$_3$OH). IR (KBr) ν cm^{-1}: 2935.1 (N-H), 2882 (glucosidic-CH), 1758 (C=O of *o*-acetyl gps of glycone moiety), 1727 (C=O), 1624 (C=N), 1055 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.9 (s, 1′-H, N-H), 7.48 (s, 2-H, CH), 6.49-7.49 (m, 3H, Ar-H), 4.85-5.04 (m, 3H, 2″, 3″, 4″-H), 4.71 (d, 1H, 1″-H, anomeric proton), 4.40 (dd, 1H, 5″-H), 3.90-4.21 (m, 2H, 6″-H), 2.34 (s, 2′-H, CH$_3$), 2.24 (s, 3′-H, CH$_3$), 2.02, 1.96, 1.98, 2.04 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.0 (C-4, C=O), 170.5 (C-atoms of acetyl C=O), 164.7 (C-7), 159.0 (C-2), 158.0 (C-9), 135.7 (C-5′), 132.1 (C-2′, C-3′), 130.8 (C-5), 117.8 (C-3), 115.1 (C-10), 108.1 (C-6), 104.1 (C-8), 102.8 (C-1″, anomeric C-atom), 75.5 (C-5″), 72.2 (C-2″), 71.5 (C-3″), 71.0 (C-4″), 66.0 (C-6″), 20.9 (C-atom, CH$_3$ of acetyl group), 11.4 (CH$_3$ of C-2′, C-3′); EI-MS *m/z* (%): 587 (M^+, 11), 256 (100), 136 (21), 91 (25). Anal. Calcd for $C_{28}H_{32}N_2O_{12}$: C, 57.34; H, 5.16; N, 4.78. Found: C, 57.31; H, 5.16; N, 4.75(%).

*7-(2,3,4,6-Tetra-o-acetyl-o-*β*-d-glucopyranosyloxy)-3-(4-phenylimidazol-2-yl)-chromone* ***4c.*** Yield 88 %, $[\alpha]_D^{25}$ = - 1.5 (*c* 0.1, CH$_3$OH). IR (KBr) ν cm^{-1}: 2924 (N-H), 2854 (glucosidic-CH), 1758 (C=O of *o*-acetyl gps of glycone moiety), 1729 (C=O), 1621 (C=N), 1037 (C-O-C), 689 (benzene monosubstituted). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.5 (s, 1′-H, NH), 7.50 (s, 2-H, CH), 7.09 (s, 2′-H, CH), 6.41-7.60 (m, 8H, Ar-H), 4.84-4.99 (m, 3H, 2″, 3″, 4″-H), 4.79 (1H, d, 1″-H, anomeric proton), 4.45 (1H, dd, 5″-H), 3.81-4.25 (m, 2H, 6″-H), 2.02, 1.94, 1.96, 2.01 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.2 (C-4, C=O), 169.9 (C-atoms of acetyl C=O), 163.8 (C-7), 158.9 (C-2), 158.0 (C-9), 139.9 (C-3′), 135.5 (C-5′), 127.5-133.5 (aromatic 6C-atom), 131.5 (C-5), 119.9 (C-2′), 117.8 (C-3), 114.8 (C-10), 109.4 (C-6), 104.1 (C-8), 101.9 (C-1″, anomeric C-atom), 75.4 (C-5″), 72.1 (C-2″), 71.7 (C-3″), 71.5 (C-4″), 66.1 (C-6″), 22.0 (C-atom, CH$_3$ of acetyl group). EI-MS *m/z* (%): 634 (M^+, 20), 304 (100), 136 (16), 91 (29). Anal. Calcd for $C_{32}H_{32}O_{12}N_2$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.54; H, 4.76; N, 4.36(%).

*7-(2,3,4,6-Tetra-o-acetyl-o-*β*-d-glucopyranosyloxy)-3-(4,5-diphenylimidazol-2-yl)-chromone* ***4d.*** Yield 80 %, $[\alpha]_D^{25}$ = - 1.9 (*c* 0.1, CH$_3$OH). IR (KBr) ν cm^{-1}: 2945 (N-H), 2855 (glucosidic-CH), 1754 (C=O of *o*-acetyl gps of glycone moiety), 1722 (C=O), 1646 (C=N), 1055 (C-O-C), 689 (benzene monosubstituted). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.8 (s, 1′-H, N-H), 7.61 (s, 2-H, CH), 6.38-7.75 (m, 13H, Ar-H), 4.86-5.02 (m, 3H, 2″, 3″, 4″-H), 4.79 (d, 1H, 1″-H, anomeric proton), 4.41 (dd, 1H, 5″-H), 3.89-4.29 (m, 2H, 6″-H), 2.02, 1.91, 1.99, 2.00 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.8 (C-4, C=O), 171.0 (C-atoms of acetyl C=O), 164.1 (C-7), 160.2 (C-2), 157.1 (C-9), 135.9 (C-5′), 131.6 (C-5), 129.5 (C-2′, C-3′), 128-133 (aromatic 6C-atom), 118.6 (C-3), 116.0 (C-10), 109.9 (C-6), 104.3 (C-8), 102.9 (C-1″, anomeric C-atom), 75.4 (C-5″), 72.1 (C-2″), 71.3 (C-4″), 71.2 (C-3″), 66.1 (C-6″), 20.7 (C-atom, CH$_3$ of acetyl group). EI-MS *m/z* (%): 711 (M^+, 14), 379 (100), 136 (11), 91 (29). Anal. Calcd for $C_{38}H_{36}N_2O_{12}$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.19; H, 4.80; N, 3.90(%).

*7-(2,3,4,6-Tetra-o-acetyl-o-*β*-d-glucopyranosyloxy)-3-[4-phenyl,5-(p-methoxyphenyl)imidazol-2-yl]-chromone* ***4e.*** Yield 89 %, $[\alpha]_D^{25}$ = - 1.5 (*c* 0.1, CH$_3$OH). IR (KBr) ν cm^{-1}: 2957 (N-H), 2857 (glucosidic-CH), 1776 (C=O of *o*-acetyl gps of glycone moiety), 1718 (C=O), 1645 (C=N), 1091 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.7 (s, 1′-H, N-H), 7.49 (s, 2-H, CH), 6.37-7.51 (m, 12H, Ar-H), 4.84-5.05 (m, 3H, 2″, 3″, 4″-H), 4.78 (d, 1H, 1″-H, anomeric proton), 4.41 (dd, 1H, 5″-H), 3.87-4.29 (m, 2H, 6″-H), 3.71 (s, 3H,

OCH_3), 2.01, 2.00, 1.97, 2.01 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 174.8 (C-4, C=O), 170.0 (C-atoms of acetyl C=O), 164.1 (C-7), 158.7 (C-2), 157.5 (C-9), 135.4 (C-5′), 131.0 (C-5), 128.9 (C-2′, C-3′), 118.9 (C-3), 115.9 (C-10), 114.5-164.5 (aromatic 12C-atom), 109.7 (C-6), 103.1 (C-8), 101.9 (C-1″, anomeric C-atom), 75.1 (C-5″), 71.9 (C-2″), 71.3 (C-3″), 71.1 (C-4″), 66.1 (C-6″), 56.1 (C-atom of OCH_3), 21.4 (C-atom, CH_3 of acetyl group). EI-MS *m/z* (%): 741 (M^+, 21), 410 (100), 136 (11), 91 (29). Anal. Calcd for $C_{39}H_{38}N_2O_{13}$: C, 63.24; H, 4.90; N, 3.78. Found: C, 63.21; H, 4.89; N, 3.77(%).

7-(2,3,4,6-Tetra-o-acetyl-o-β-D-glucopyranosyloxy)-3-[4,5-di(o-chlorophenyl)imidazol-2-yl]-chromone ***4f.*** Yield 75 %, $[\alpha]_D^{25}$ = - 2.4 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 2935 (N-H), 2859 (glucosidic-CH), 1768 (C=O of *o*-acetyl gps of glycone moiety), 1717 (C=O), 1631 (C=N), 1074 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.1 (s, 1′-H, N-H), 7.49 (s, 2-H, CH), 6.44-7.41 (m, 11H, Ar-H), 4.81-4.99 (m, 3H, 2″, 3″, 4″-H), 4.77 (d, 1H, 1″-H, anomeric proton), 4.41 (dd, 1H, 5″-H), 3.84-4.20 (m, 2H, 6″-H), 2.00, 2.01, 1.98, 2.04 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.1 (C-4, C=O), 171.0 (C-atoms of acetyl C=O), 163.7 (C-7), 159.0 (C-2), 158.2 (C-9), 135.8 (C-5′), 131.6 (C-5), 128.9 (C-2′, C-3′), 125-135 (aromatic 12C-atom), 119.0 (C-3), 115.8 (C-10), 109.8 (C-6), 103.4 (C-8), 101.7 (C-1″, anomeric C-atom), 74.9 (C-5″), 73.1 (C-2″), 71.4 (C-3″), 71.1 (C-4″), 66.0 (C-6″), 21.4 (C-atom, CH_3 of acetyl group). EI-MS *m/z* (%): 780 (M^+, 18), 449 (100), 136 (27), 91 (19). Anal. Calcd for $C_{38}H_{34}N_2O_{12}Cl_2$: C, 58.55; H, 4.14; N, 3.59. Found: C, 58.49; H, 4.07; N, 3.52(%).

7-(2,3,4,6-Tetra-o-acetyl-o-β-D-glucopyranosyloxy)-3-[4,5-di(p-chlorophenyl)imidazol-2-yl]-chromone ***4g.*** Yield 83 %, $[\alpha]_D^{25}$ = - 4.7 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 2975 (N-H), 2861 (glucosidic-CH), 1725 (C=O of *o*-acetyl gps of glycone moiety), 1700 (C=O), 1614 (C=N), 1094 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.8 (s, 1′-H, N-H), 7.41 (s, 2-H, CH), 6.41-7.49 (m, 11H, Ar-H), 4.78-4.98 (m, 3H, 2″, 3″, 4″-H), 4.87 (d, 1H, 1″-H, anomeric proton), 4.45 (dd, 1H, 5″-H), 3.81-4.26 (m, 2H, 6″-H), 2.01, 2.02, 1.97, 2.03 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.5 (C-4, C=O), 171.8 (C-atoms of acetyl C=O), 163.1 (C-7), 159.7 (C-2), 158.8 (C-9), 135.1 (C-5′), 131.2 (C-5), 129.3 (C-2′, C-3′), 125.7-135.9 (aromatic 12C-atom), 119.2 (C-3), 115.1 (C-10), 109.6 (C-6), 103.9 (C-8), 101.1 (C-1″, anomeric C-atom), 75.2 (C-5″), 73.6 (C-2″), 71.3 (C-3″), 70.2 (C-4″), 66.3 (C-6″), 21.1 (C-atom, CH_3 of acetyl group). EI-MS *m/z* (%): 780 (M^+, 23), 449 (100), 136 (33), 91 (25). Anal. Calcd for $C_{38}H_{34}N_2O_{12}Cl_2$: C, 58.55; H, 4.14; N, 3.59. Found: C, 58.47; H, 4.07; N, 3.51(%).

7-(2,3,4,6-Tetra-o-acetyl-o-β-D-glucopyranosyloxy)-3-[4,5-di(N,N-dimethylaminophenyl)imidazol-2-yl]-chromone ***4h***. Yield 80 %, $[\alpha]_D^{25}$ = - 3.2 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 2989 (N-H), 2867 (glucosidic-CH), 1729 (C=O of *o*-acetyl gps of glycone moiety), 1705 (C=O), 1623 (C=N), 1110 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.7 (s, 1′-H, N-H), 7.44 (s, 2-H, CH), 6.46-7.41 (m, 11H, Ar-H), 4.72-4.96 (m, 3H, 2″, 3″, 4″-H), 4.89 (d, 1H, 1″-H, anomeric proton), 4.48 (dd, 1H, 5″-H), 3.86-4.29 (m, 2H, 6″-H), 2.83 (s, 6H, $N(CH_3)_2$), 2.76 (s, 6H, $N(CH_3)_2$), 1.98, 2.01, 2.04, 2.00 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.1 (C-4, C=O), 171.3 (C-atoms of acetyl C=O), 163.4 (C-7), 159.2 (C-2), 158.2 (C-9), 135.7 (C-5′), 131.0 (C-5), 129.0 (C-2′, C-3′), 125.1-135.4 (aromatic 12C-atom), 119.1 (C-3), 115.8 (C-10), 109.3 (C-6), 103.3 (C-8), 101.7 (C-1″, anomeric C-atom), 75.7 (C-5″), 73.9 (C-2″), 71.4 (C-3″), 70.8 (C-4″), 66.5 (C-6″), 40.5 ($N(CH_3)_2$), 40.2 ($N(CH_3)_2$), 21.3 (C-atom, CH_3 of acetyl group). Anal. Calcd for $C_{42}H_{44}N_4O_{12}$: C, 63.31; H, 5.57; N, 7.03. Found: C, 63.22; H, 5.50; N, 6.97(%).

7-(2,3,4,6-Tetra-o-acetyl-o-β-D-glucopyranosyloxy)-3-[4,5-di-(p-methylphenyl)imidazol-2-yl]-chromone ***4i***. Yield 85%, $[\alpha]_D^{25}$ = -2.9 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 2979 (N-H), 2860 (glucosidic-CH), 1733 (C=O of *o*-acetyl gps of glycone moiety), 1712 (C=O), 1621 (C=N), 1098 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.3 (s, 1′-H, N-H), 7.45 (s, 2-H, CH), 6.36-7.55 (m, 11H, Ar-H), 4.72-4.97 (m, 3H, 2″, 3″, 4″-H), 4.88 (d, 1H, 1″-H, anomeric proton), 4.49 (dd, 1H, 5″-H), 3.80-4.29 (m, 2H, 6″-H), 2.23 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.01, 2.02, 1.99, 2.03 (s, 3H, OAc). ^{13}C NMR (DMSO-d_6) δ_C ppm: 175.0 (C-4, C=O), 171.1 (C-atoms of acetyl C=O), 163.4 (C-7), 159.2 (C-2), 158.6 (C-9), 135.9 (C-5′), 131.7 (C-5), 129.0 (C-2′, C-3′), 125.1-135.4 (aromatic 12C-atom), 119.8 (C-3), 115.8 (C-10), 109.2 (C-6), 103.4 (C-8), 101.8 (C-1″, anomeric C-atom), 75.7 (C-5″), 73.1 (C-2″), 71.9 (C-3″), 70.5 (C-4″), 66.8 (C-6″), 24.6 (C-atom of CH_3), 23.8 (C-atom of CH_3), 21.9 (C-atom, CH_3 of acetyl group). Anal. Calcd for $C_{40}H_{38}N_2O_{12}$: C, 65.03; H, 5.18; N, 3.79. Found: C, 64.91; H, 5.11; N, 3.71(%).

General procedure for the preparation of compounds ***5a-i.*** The mixture of 2,3,4,6-tetra-*o*-acetyl-7-*o*-*β*-*D*-glucopyranosyloxy-3-(4,5-disubstituted imidazol-2-yl)-chromones **4a-i** (0.109 mmol), dry methanol (2 ml) and anhydrous zinc acetate (0.126 mmol) was refluxed for 7-9 h (monitored by TLC). After cooled down at room temperature, it was filtered through cation exchanged resin; the solvent was removed under vacuum. The residue was purified by silica gel chromatography ($CHCl_3$, MeOH, 12:1 v/v) to get titled compound.

7-o-β-D-Glucopyranosyloxy-3-(imidazol-2-yl)-chromone ***5a.*** Yield 90 %, $[\alpha]_D^{25}$ = - 9.1 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 3412 (br, OH peak of carbohydrate residue), 2929 (N-H), 2853 (glucosidic-CH), 1599 (C=O), 1445 (C=N), 1089 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.7 (s, 1′-H, N-H), 7.51 (s, 2-H, CH), 7.06 (d, 2′-H, 3′-H) (CH), 6.37-7.55 (m, 3H, Ar-H), 5.74 (d, 1″-H, anomeric proton), 3.44-4.72 (m, 6H, β-*D*-glucopyranosyl ring). ^{13}C NMR (DMSO-d_6) δ_C ppm: 174.7 (C-4, C=O), 163.8 (C-7), 159.6 (C-2), 158.1 (C-9), 136.1 (C-5′), 130.8 (C-5), 127.8 (C-2′, C-3′), 118.2 (C-3), 116.2 (C-10), 109.9 (C-6), 106.0 (C-1″, anomeric C-atom), 104.0 (C-8), 82.1 (C-5″), 77.6 (C-3″), 74.9 (C-2″), 73.1 (C-4″), 64.0 (C-6″). EI-MS *m/z* (%): 391 ($[M+1]^+$, 10), 228 (100), 136 (15), 91 (25). Anal. Calcd for $C_{18}H_{16}N_2O_8$: C, 55.39; H, 4.65; N, 7.18. Found: C, 55.35; H, 4.66; N, 7.16(%).

7-o-β-D-Glucopyranosyloxy-3-(4,5-dimethylimidazol-2-yl)-chromone ***5b***. Yield 91 %, $[\alpha]_D^{25}$ = - 10.1 (*c* 0.1, CH_3OH). IR (KBr) ν cm^{-1}: 3446 (br, OH peak of carbohydrate residue), 2958 (N-H), 2856 (glucosidic-CH), 1598 (C=O), 1414 (C=N), 1092 (C-O-C); ^{1}H NMR (DMSO-d_6) δ_H ppm: 13.2 (s, 1′-H, N-H), 7.56 (s, 2-H, CH), 6.41-7.49 (m, 3H, Ar-H), 5.69 (d, 1″-H, anomeric proton), 3.45-4.95 (m, 6H, β-*D*-glucopyranosyl ring), 2.34 (s, 2′-H, CH_3), 2.19 (s, 3′-H, CH_3). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.0 (C-4, C=O), 163.5 (C-7), 159.6 (C-2), 158.1 (C-9), 135.6 (C-5′), 132.1 (C-2′,C-3′), 131.1 (C-5), 118.0 (C-3), 115.1 (C-10), 109.3 (C-6), 105.0 (C-1″, anomeric C-atom), 103.5 (C-8), 81.1 (C-5″), 77.7 (C-3″), 75.9 (C-2″), 73.0 (C-4″), 65.8 (C-6″), 11.9 (CH_3 of C-2′, C-3′). EI-MS *m/z* (%): 419 ($[M+1]^+$, 7), 256 (100), 163 (18), 136 (28), 91 (16). Anal. Calcd for $C_{20}H_{20}N_2O_8$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.37; H, 5.27; N, 6.67(%).

7-o-β-D-Glucopyranosyloxy-3-(4-phenylimidazol-2-yl)-chromone ***5c.*** Yield 96 %, $[\alpha]_D^{25}$ = - 15.5 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3400 (br, OH peak of carbohydrate residue), 2925 (N-H), 2854 (glucosidic-CH), 1592 (C=O), 1404 (C=N), 1071 (C-O-C), 689 (benzene monosubstituted). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.7 (s, 1′-H, NH), 7.48 (s, 2-H, CH), 7.11 (s, 2′-H, CH), 6.43-8.08 (m, 8H, Ar-H), 5.85 (d, 1″-H, anomeric proton), 3.41-4.70 (m, 6H, β-*D*-glucopyranosyl ring). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.2 (C-4, C=O), 164.7 (C-7), 159.1 (C-2), 157.7 (C-9), 140.1 (C-3′), 136.4 (C-5′), 131.0 (C-5), 127.0-133.5 (aromatic 6C-atom), 121.4 (C-2′), 119.4 (C-3), 114.9 (C-10), 109.1 (C-6), 105.4 (C-1″, anomeric C-atom), 103.1 (C-8), 81.2 (C-5″), 77.0 (C-3″), 75.1 (C-2″), 73.9 (C-4″), 65.7 (C-6″). EI-MS *m/z* (%): 467 ($[M+1]^+$, 4), 304 (100), 227 (20), 163 (21), 136 (18), 91 (30), 77 (18). Anal. Calcd for $C_{24}H_{20}N_2O_8$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.54; H, 4.76; N, 4.36(%).

7-o-β-D-Glucopyranosyloxy-3-(4,5-diphenylimidazol-2-yl)-chromone ***5d***. Yield 92 %, $[\alpha]_D^{25}$ = - 11.9 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3428 (br, OH peak of carbohydrate residue), 2929 (N-H), 2858 (glucosidic-CH), 1597 (C=O), 1429 (C=N), 1100 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.8 (s, 1′-H, N-H), 7.59 (s, 2-H, CH), 6.50-7.75 (m, 13H, Ar-H), 5.80 (d, 1″-H, anomeric proton), 3.43-4.78 (m, 6H, β-D-glucopyranosyl ring). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (C-4, C=O), 164.5 (C-7), 160.2 (C-2), 157.1 (C-9), 136.5 (C-5′), 130.9 (C-5), 129.6 (C-2′, C-3′), 127.4-133.9 (aromatic 6C-atom), 118.9 (C-3), 115.1 (C-10), 109.5 (C-6), 106.2 (C-1″, anomeric C-atom), 104.1 (C-8), 81.4 (C-5″), 77.2 (C-3″), 75.2 (C-2″), 73.9 (C-4″), 64.9 (C-6″). EI-MS *m/z* (%): 542 (M^+, 9), 379 (100), 227 (11), 163 (41), 136 (19), 91 (21), 77 (20). Anal. Calcd for $C_{30}H_{24}N_2O_8$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.19; H, 4.80; N, 3.90(%).

7-o-β-D-Glucopyranosyloxy-3-[4-phenyl,5-(p-methoxyphenyl)imidazol-2-yl]-chromone ***5e.*** Yield 89 %, $[\alpha]_D^{25}$ = - 9.8 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3411 (br, OH peak of carbohydrate residue), 2944 (N-H), 2856 (glucosidic-CH), 1593 (C=O), 1415 (C=N), 1099 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.9 (s, 1′-H, N-H), 7.51 (s, 2-H, CH), 6.39-7.48 (m, 12H, Ar-H), 5.54 (d, 1″-H, anomeric proton), 3.45-4.78 (m, 6H, β-D-glucopyranosyl ring), 3.70 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (C-4, C=O) 163.8 (C-7), 158.8 (C-2), 157.4 (C-9), 136.1 (C-5′), 131.4 (C-5), 129.1 (C-2′, C-3′), 118.1 (C-3), 115.3 (C-10), 115-164 (aromatic 12C-atom), 110.1 (C-6), 106.1 (C-1″, anomeric C-atom), 103.5 (C-8), 81.1 (C-5″), 78.1 (C-3″), 74.7 (C-2″), 73.1 (C-4″), 64.6 (C-6″), 56.0 (C-atom of OCH_3). EI-MS *m/z* (%): 573 ($[M+1]^+$, 11), 410 (100), 163 (29), 91 (19). Anal. Calcd for $C_{31}H_{26}N_2O_8$: C, 63.03; H, 4.93; N, 4.89. Found: C, 65.01; H, 4.94; N, 4.88(%).

7-o-β-D-Glucopyranosyloxy-3-[4,5-di(o-chlorophenyl) imidazol-2-yl]-chromone ***5f.*** Yield 85 %, $[\alpha]_D^{25}$ = - 12.4 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3454 (br, OH peak of carbohydrate residue), 2928 (N-H), 2852 (glucosidic-CH), 1591 (C=O), 1420 (C=N), 1095 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.6 (s, 1′-H, N-H), 7.55 (s, 2-H, CH), 6.40-7.51 (m, 11H, Ar-H), 5.68 (d, 1″-H, anomeric proton), 3.41-4.74 (m, 6H, β-D-glucopyranosyl ring). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.1 (C-4, C=O), 165.1 (C-7), 159.0 (C-2), 158.2 (C-9), 135.6 (C-5′), 130.9 (C-5), 129.0 (C-2′, C-3′), 126.5-134.5 (aromatic 12C-atom), 117.8 (C-3), 115.1 (C-10), 109.9 (C-6), 106.2 (C-1″, anomeric C-atom), 104.3 (C-8), 82.4 (C-5″), 77.2 (C-3″), 75.8 (C-2″), 73.1 (C-4″), 64.1 (C-6″). EI-MS *m/z* (%): 612 ($[M+1]^+$, 9), 449 (100), 163 (19), 91 (23). Anal. Calcd for $C_{30}H_{24}N_2O_8Cl_2$: C, 58.93; H, 3.96; N, 4.58. Found: C, 58.90; H, 3.95; N, 4.55(%).

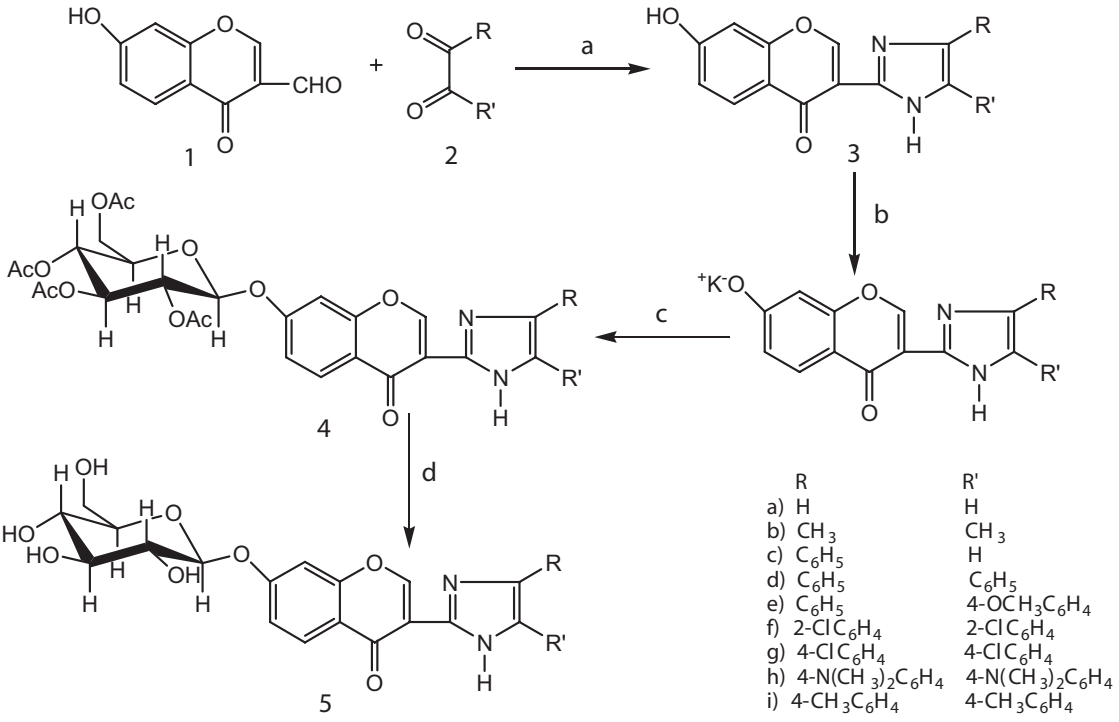
7-o-β-D-Glucopyranosyloxy-3-[4,5-di(p-chlorophenyl) imidazol-2-yl]-chromone ***5g.*** Yield 83 %, $[\alpha]_D^{25}$ = - 13.1 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3336 (br, OH peak of carbohydrate residue), 2988 (N-H), 2852 (glucosidic-CH), 1645 (C=O), 1443 (C=N), 1099 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.9 (s, 1′-H, N-H), 7.50 (s, 2-H, CH), 6.33-7.55 (m, 11H, Ar-H), 5.78 (d, 1″-H, anomeric proton), 3.45-4.75 (m, 6H, β-D-glucopyranosyl ring). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.3 (C-4, C=O), 165.3 (C-7), 159.6 (C-2), 158.8 (C-9), 135.1 (C-5′), 130.3 (C-5), 129.4 (C-2′, C-3′), 126.2-134.4 (aromatic 12C-atom), 117.4 (C-3), 115.7 (C-10), 109.4 (C-6), 106.8 (C-1″, anomeric C-atom), 104.9 (C-8), 82.2 (C-5″), 77.5 (C-3″), 75.2 (C-2″), 73.6 (C-4″), 64.8 (C-6″). EI-MS *m/z* (%): 612 ($[M+1]^+$, 14), 449 (100), 163 (23), 91 (34). Anal. Calcd for $C_{30}H_{24}N_2O_8Cl_2$: C, 58.93; H, 3.96; N, 4.58. Found: C, 58.85; H, 3.90; N, 4.51(%).

7-o-β-D-Glucopyranosyloxy-3-[4,5-di(N,N-dimethylamino-phenyl)imidazol-2-yl]-chromone ***5h.*** Yield 91 %, $[\alpha]_D^{25}$ = - 9.2 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3345 (br, OH peak of carbohydrate residue), 2967 (N-H), 2859 (glucosidic-CH), 1634 (C=O), 1432 (C=N), 1150 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 11.7 (s, 1′-H, N-H), 7.50 (s, 2-H, CH), 6.45-7.56 (m, 11H, Ar-H), 5.71 (d, 1″-H, anomeric proton), 3.35-4.74 (m, 6H, β-D-glucopyranosyl ring), 2.87 (s, 6H, $N(CH_3)_2$), 2.81 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.3 (C-4, C=O), 165.5 (C-7), 158.6 (C-2), 158.6 (C-9), 135.1 (C-5′), 130.5 (C-5), 129.3 (C-2′, C-3′), 125.2-136.3 (aromatic 12C-atom), 117.2 (C-3), 115.8 (C-10), 110.2 (C-6), 106.7 (C-1″, anomeric C-atom), 104.6 (C-8), 82.9 (C-5″), 77.9 (C-3″), 75.3 (C-2″), 73.7 (C-4″), 64.6 (C-6″), 40.7 ($N(CH_3)_2$), 40.1 ($N(CH_3)_2$). Anal. Calcd for $C_{34}H_{36}N_4O_8$: C, 64.96; H, 5.77; N, 8.91. Found: C, 64.85; H, 5.69; N, 8.82(%).

7-o-β-D-Glucopyranosyloxy-3-[4,5-di(p-methylphenyl)-imidazol-2-yl]-chromone ***5i***. Yield 96 %, $[\alpha]_D^{25}$ = - 11.1 (*c* 0.1, DMSO). IR (KBr) ν cm^{-1}: 3234 (br, OH peak of carbohydrate residue), 2985 (N-H), 2857 (glucosidic-CH), 1672 (C=O), 1443 (C=N), 1096 (C-O-C). ^{1}H NMR (DMSO-d_6) δ_H ppm: 12.2 (s, 1′-H, N-H), 7.59 (s, 2-H, CH), 6.37-7.45 (m, 11H, Ar-H), 5.79 (d, 1″-H, anomeric proton), 3.45-4.79 (m, 6H, β-D-glucopyranosyl ring), 2.28 (s, 3H, CH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ_C ppm: 176.5 (C-4, C=O), 165.4 (C-7), 159.3 (C-2), 158.9 (C-9), 135.2 (C-5′), 130.4 (C-5), 129.9 (C-2′, C-3′), 126-134.5 (aromatic 12C-atom), 117.2 (C-3), 115.6 (C-10), 109.3 (C-6), 106.8 (C-1″, anomeric C-atom), 104.7 (C-8), 82.1 (C-5″), 77.7 (C-3″), 75.4 (C-2″), 73.6 (C-4″), 64.8 (C-6″), 24.2 (C-atom of CH_3), 23.3 (C-atom of CH_3). Anal. Calcd for $C_{32}H_{30}N_2O_8$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.25; H, 5.21; N, 4.81(%).

Results and Discussion

Our synthetic pathway is outlined in Scheme 1. During the course of our present research work, the starting compound 7-hydroxy-3-formyl chromone **1** was prepared by Vilsmeier-Haack reaction from resacetophenone.[25,27] The condensation of **1** with various 1,2-dicarbonyl compounds **2** in the presence of anhydrous CH_3COONH_4 in glacial acetic acid undergoes cyclisation results in the formation of 7-hydroxy-3-(4,5-disubstituted imidazol-2-yl)-4*H*-chromen-4-ones[28] (**3a-i**). The IR spectrum of **3a** showed a broad peak at 3400 cm^{-1} due to the OH stretch; the peak at 3064 cm^{-1} was appeared due to N-H stretch; a strong absorption at 1622 cm^{-1} was assigned to C=O stretch; the peaks at 1455 and 1171 cm^{-1} were due to C=N and C-O-C stretches respectively. The ^{1}H NMR spectrum exhibited three singlets at δ 5.12, 7.26, and 12.9 which readily recognised as arising from OH, C-H, and N-H respectively. The characteristic multiplets for the aromatic protons are located at δ = 6.40-7.49. The ^{13}C NMR spectrum of **3a** showed 12 distinctive resonances in agreement with the proposed structure. The potassium salts of **3a-i** for *o*-glucosydation were prepared by the action of anhydrous K_2CO_3 in the mixture of DMF and acetone (3:2 v/v) as a solvent. An interaction between the potassium salt and α-acetobromoglucose as glucosyl donor in the presence of dodecyltrimethylammonium bromide (DTMAB) as a phase transfer catalyst. This gives rise 2,3,4,6-tetra-*o*-acetyl-*β*-D-glucopyranosyloxy-3-(4,5-disubstituted imidazol-2-yl)-4*H*-chromen-4-ones **4a-i**. The absence of IR band in **4a** due to OH stretch at 3400 cm^{-1} is indicating the formation of product. Further, the peaks at 3056 and 2924 cm^{-1} were due to the C-H and N-H stretches respectively. The C=O stretch peak was found to be shifted to 1729 cm^{-1}. A strong absorption at 1757 cm^{-1} was assigned to C=O stretch of *o*-acetyl groups of glucose moiety. The peaks at 1621 and 1037 cm^{-1} were attributed to the C=N and C-O-C stretches respectively. A sharp peak at 2853 cm^{-1} was assigned to glucosidic C-H stretch. The ^{1}H NMR spectrum exhibited



Scheme 1. Synthesis of 7-*o*-*β*-*D*-glucopyranosyloxy-3-(4, 5-disubstituted imidazol-2-yl)-4*H*-chromen-4-ones **5**. Reagents: (a) CH_3COONH_4, CH_3COOH; (b) K_2CO_3, DMF, $(CH_3)_2CO$; (c) DTMAB, α-acetobromoglucose; (d) $Zn(CH_3COO)_2$, MeOH.

signals at δ 12.5 (s, 1′-H, N-H), 7.46 (s, 2-H, CH), 7.15 (d, 2′-H, 3′-H) (CH), 6.44-7.43 (m, 3H, Ar-H), 4.87-5.00 (m, 3H, 2″, 3″, 4″-H), 4.76 (d, 1H, 1″-H, anomeric proton), 4.39 (dd, 1H, 5″-H), 3.86-4.24 (m, 2H, 6″-H), 2.01, 1.95, 1.99, 2.05 (s, 3H, OAc). Similarly, ^{13}C data of the acetylated β-glucosides (**4a-i**) were in agreement with the assigned structures.

We tried to deacetylate of **4a-i** by standard procedure using NaOMe/MeOH;[29] however, we found that the strong basic condition resulted in cleavage of the isoflavone's C-ring, while the anhydrous zinc acetate in absolute methanol system led to significant deglycosylation. Finally, complete deacetylation of **4a-i** was achieved by using anhydrous zinc acetate in absolute methanol yielded corresponding *o*-*β*-*D*-glucosides **5a-i** in good yields. The IR spectrum of **5a** showed the presence of characteristic absorption peaks at 3412, 2929, 2853, 1599, 1445, and 1089 due to OH of carbohydrate residue, N-H, glucosidic C-H, C=O, C=N, and ether linkage respectively. The ^1H NMR data showed the presence of carbohydrate moiety. The chemical shift of the anomeric proton show β-linkage at δ 5.74 (C-H) indicating the linkage of carbohydrate unit to C-7 position of the aglycone. The compounds gave satisfactory C, H and N analysis. The mass spectrum of **5a** displayed the molecular ion peak $[M+1]^+$ at *m/z* = 391, which is consistent with its proposed structure.

Conclusions

In conclusion we have synthesized the newly synthesized glucosides of 7-hydroxy-3-(4,5-disubstituted imidazol-2-yl)-4*H*-chromen-4-ones with promising yield.

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