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Synthesis and biological activities of new hydroxy-3-pyrazolyl-4*H*-chromen-4-ones and their *O*-glucosides

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The synthesis of a number of 7-hydroxy-3-pyrazolyl-chromen-4*H*-ones and their *O*-glucosides has been described. 7-Hydoxy-3-formyl chromen-4*H*-one **1** on condensation with substituted acetophenones in the presence of piperidine in dry alcohol affords 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **2** which on cyclization with phenyl hydrazine hydrochloride leads to the formation of 7-hydroxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **3**. 7-*O*-β-D-Glucopyranosyloxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **5** have been synthesized by the reaction of 2, 3, 4, 6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with potassium salt of **3** followed by deacetylation with $Zn(CH_3COO)_2$ in absolute methanol. Some of the newly synthesized compounds have been screened for their antimicrobial and antioxidant activity.

Keywords: Chromones, pyrazoles, glucopyranosyl bromide, glucosylation, *O*-β-D-glucosides, deacetylation, biological activity

Flavonoids constitute one of the most active classes of compounds possessing diverse pharmacological and microbial activity[1]. The widespread flavonoids act as various functional secondary metabolites in plants. Literature survey reveals that chromones show anticancer[2], anti-HIV[3] and antioxidant properties[4]. Pyrazoles are quite popular in the field of medicine and agro chemistry. A number of pyrazole derivatives have been reported to possess interesting biological activities like anti-inflammatory[5], antimicrobial[6] and antiprotozoal activities[7]. In addition, pyrazole is found widely as a core structure in a large variety of compounds that exhibit important biological activity[8]. Many organic compounds containing carbohydrate[9] exhibit a wide variety of biological and therapeutic properties[10]. Another large group of carbohydrate containing therapeutics are the nucleoside analogs. Nucleosides which are also glycosides occur in nucleic acids. Several O-, N- and C-glycosides have been isolated from other natural sources[11]. These compounds have a wide range of biological activities including antibacterial, antifungal, antiviral and antitumour activities. As a result, the formation of the glycosidic linkage continues to be a dominant theme in the carbohydrate chemistry[12]. 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[13].

In view of these observations and in continuation of our work[14] on chromone based heterocycles, it was considered of interest to synthesize new chemical entities incorporating the three active pharmacophores namely chromone, pyrazole and glucose moiety in a single molecular framework as new possible biological active compounds. Herein we report the synthesis and biological activity of chromones containing pyrazole, a heterocycle at position 3 and glucose residue at position 7, starting from the corresponding 7-hydroxy-3-formyl-4*H*-chromen-4-one and their *O*-β-D-glucosides.

Results and Discussion

To achieve targeted compound, the required starting compound 7-hydroxy-3-formyl-4*H*-chromen-4-one **1** was prepared from resacetophenone[15]. The compound **1** on condensation[16] with substituted acetophenones in the presence of freshly distilled piperidine in absolute alcohol as in the formation of 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **2**. The ^{1}H NMR spectrum of the said compound showed the peaks at δ 7.70 (d, 1H, CH),

7.14 (s, 2-H, CH), 6.1 (d, 1H, CH), 6.34-7.78 (m, 8H, Ar-H), 4.98 (s, 1H, OH). There was no peak due to –CHO group. The said compound was also confirmed by ^{13}C NMR. Cyclisation[17] of α, β-unsaturated compounds **2** with phenyl hydrazine hydrochloride in aprotic solvent like DMF afforded 7-hydroxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **3** **(Scheme I)**.

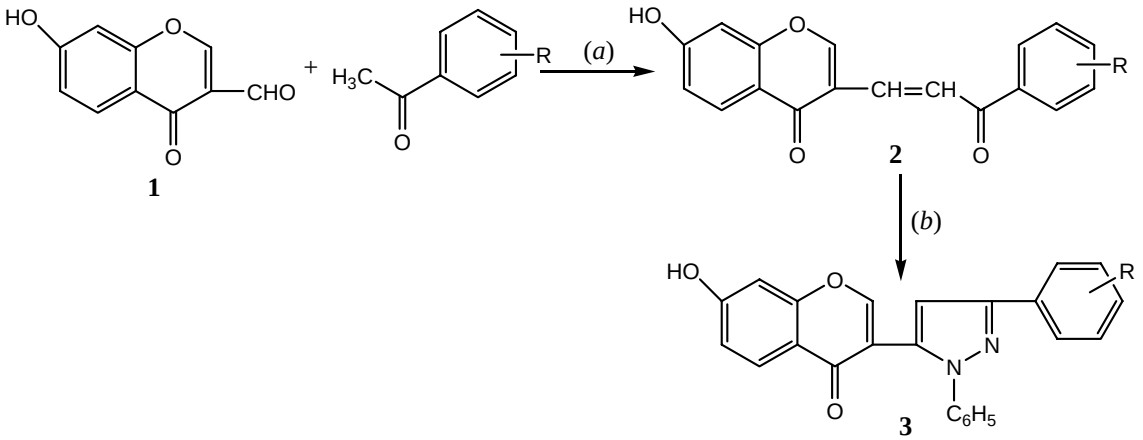
The pentacetate derivative of glucose was readily prepared in crystalline form as the α-anomer by standard procedure[18]. The peracetylated sugar is then converted to α-acetobromoglucose. It acts as a glucosyl donor for the glucosylation[19] of **3** (its potassium salt). The reaction has been carried out using anhydrous K_2CO_3 under argon atmosphere in dry acetonitrile as solvent in the presence of 18-crown-6 ether as a catalyst yielded 2, 3, 4, 6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **4**. The absence of IR band at 3100-3500 cm^{-1} (due to OH stretch) indicates the formation of product **4a**. Further, the peaks at 3042, 2361 cm^{-1} were due to the Ar-CH stretch. The C=O stretch peak was found to be shifted to 1626 cm^{-1}. A strong absorption at 1760 cm^{-1} was assigned to C=O stretch of *O*-acetyl groups of glucose moiety. The peak at 1027 cm^{-1} was attributed to the C-O-C stretch. A sharp peak at 2854 cm^{-1} was assigned to glucosidic -CH stretch. The ^1H and ^{13}C NMR data of the acetylated β-glucosides **4a-i** were in agreement with the assigned structures.

7-*O*-β-D-Glucopyranosyloxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **5** were prepared by the deacetylation of acetylated β-glucosides **4** with anhydrous zinc acetate in absolute methanol[20] **(Scheme II)**. The IR spectrum of **5a** showed the presence of characteristic absorption peaks at 3401 (br, OH peak of carbohydrate residue), 2853 (glucosidic-CH), 1720 (C=O), 1032 (C-O-C, ether linkage) cm^{-1}, indicating the formation *O*-β-D-glucoside. This was also confirmed by its ^1H NMR, ^{13}C NMR and EI-MS data. The ^1H NMR and ^{13}C NMR data show the presence of carbohydrate moiety. The chemical shift of the anomeric proton shows β-linkage at δ 5.77 (-CH) indicating the linkage of carbohydrate unit to C-7 position of the aglycone. Signals due to hydroxyl protons of the carbohydrate were not observed because of the fast exchange of all non-hydrogen bonded OH groups, and the acidic phenolic functions.

In EI-MS studies the molecular ion peak at *m*/*z* 544 $(M+1)^+$ was dominated by *m*/*z* 381 (100%) with the loss of 163 amu corresponding to the loss of an intact anhydro-sugar moiety. Also the molecular ion at *m*/*z* 544 $(M+1)^+$ confirmed the molecular formula of the glucoside. The compounds gave satisfactory C, H and N analysis**.**

Biological activity

Compounds **3a-i** and **5a-i** were screened for various biological screening programmes. The various screening programmes carried out includes the *in vitro* antibacterial activity against *Escherichia coli*, *Klebisilla aerogens*, *Staphyllococcus aureus* and *Bacillus substilis* and *in vitro* antifungal activity against *A. niger* and *C. albicans* fungi using the cup plate diffusion method[21] by measuring the inhibition zones in mm. The comparative studies of the aglycones and glucosides have been observed by using standard ciprofloxacin, sulphacetamide for bacteria and gentamycin, clotrimazole (100μg/mL) for fungi. The test compounds were dissolved in DMSO at a concentration of 100μg/mL. Most of the



Scheme I — (*a*) $C_5H_{11}N$, dry absolute C_2H_5OH; (*b*) $C_6H_5NHNH_2$.HCl, DMF

compounds exhibited mild to moderate antibacterial activity as well as antifungal activity against all the microbes tested. Similarly *in vitro* free radical scavenging activities of glucosides were evaluated by DPPH assay method[22] and most of the compounds were found active at 1mg/mL concentration. Percentage scavenging of DPPH radical was calculated using the formula: % Scavenging of DPPH = [(Control - Test) / Control] × 100.

Conclusion

In the present work, various glucosides of 7-hydroxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones were synthesised and evaluated their *in-vitro* antimicrobial activity and anti-oxidant activity. Biological results revealed that the new glucosides of 7-hydroxy-3-pyrazolyl chromones show greater pharmacological significance than that of aglycones.

Experimental Section

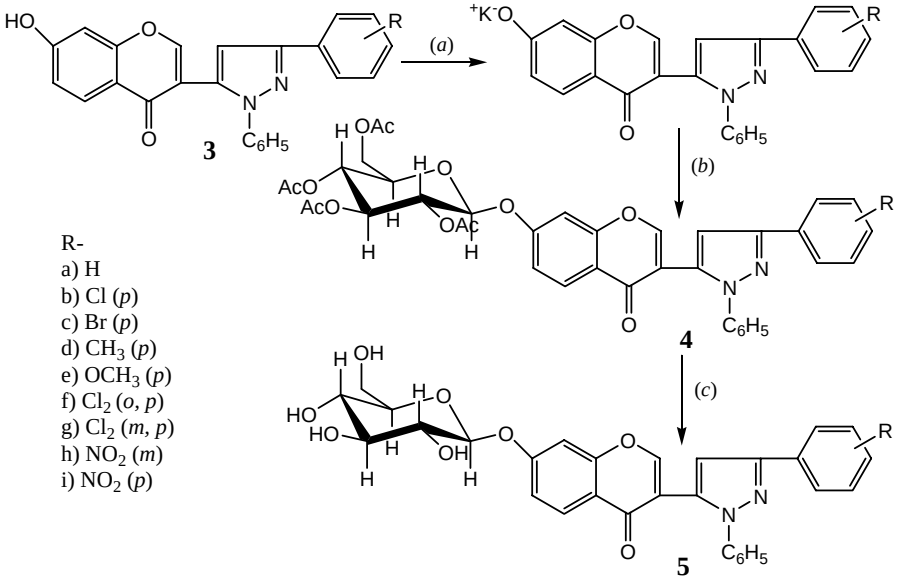
All melting points were determined in open capillary tube on a liquid paraffin-bath and are uncorrected. The IR spectra were recorded using (KBr) on a Perkin-Elmer FT-IR infrared spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker II-400 NMR spectrometer, using TMS as an internal reference in DMSO-d_6 as a solvent. The chemical shifts (δ) were expressed in ppm. EI-MS were determined on Hitachi Perkin-Elmer RMU 6D mass spectrometer. Elemental analyses were determined using the Perkin-Elmer 2400 CHN analyzer. Purity of the compounds was checked on silica gel plates using iodine vapour as a visualizing agent.

7-Hydroxy-3-formyl chromone 1

In dry DMF (121 mL) in three necked flask, $POCl_3$ (75 mL, 0.49 mole) was added slowly with vigorous stirring at 50°C. Heating and stirring was continued for 2 hr at 45-55°C. The solution of resacetophenone (18.24 g, 0.12 moles) in DMF (25 mL) was then slowly added with stirring at 50°C and the stirring was continued for 2 hr. After cooling, the mixture was kept overnight at room temp. and diluted slowly by adding ice-cold water (500 mL) and stirred again for 6 hr. The red crystalline product obtained was filtered off and recrystallized from alcohol, yield 45 g (78%), m.p. 269°C. Its alcoholic solution gives violet coloration with neutral $FeCl_3$. IR (KBr): 3428 (phenolic OH), 3087, 2363 (Ar-CH), 2773 (-CH *str*, CHO), 1685 (C=O), 1614 (C=C), 1093 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 9.59 (s, 1H, CHO), 8.82 (s, 2-H, CH), 6.8-8.0 (m, 3H, Ar-H), 4.95 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 188.1 (s, CHO of C-3), 174.9 (s, C-4, C=O), 171.0 (s, C-2), 161.2 (s, C-7), 157.9 (s, C-9), 131.4 (s, C-5), 115.7 (s, C-3, C-CHO), 114.0 (s, C-10), 109.4 (s, C-6), 104.8 (s, C-8).

General procedure for the preparation of 7-hydroxy-3-(3-aryl-3-oxoprop-1-enyl)-4*H*-chromen-4-ones 2a-i

A mixture of 7-hydroxy-3-formyl-4*H*-chromen-4-one (0.01 moles), substituted acetophenone (0.012



Scheme II — (*a*) K_2CO_3, CH_3CN, argon atmosphere; (*b*) α-acetobromoglucose, 18-crown-6; (*c*) $Zn(OAc)_2$, MeOH

moles), ethyl alcohol (100 mL) and one drop of piperidine were warmed for 2 hr. It was cooled to 0°C; the light yellow solid obtained was filtered, washed with distilled water, dried and crystallized from benzene/ethanol. It gave red colour with conc. H_2SO_4. The physical and analytical data of compounds are given in **Table I**. The spectral data of various **2a-i** are described below.

2a: IR (KBr): 3348 (br, OH), 3077, 2361 (Ar-CH), 1695 (C=O), 1458 (CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.70 (d, 1H, CH), 7.14 (s, 2-H, CH), 6.1 (d, 1H, CH), 6.34-7.78 (m, 8H, Ar-H), 4.98 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 188.8 (s, C-2', CO), 178.1 (s, C-4, C=O), 164.8 (s, C-7), 157.8 (s, C-9), 149.0 (s, C-2), 142.4 (s, C-1', CH), 138.0 (s, C-1"), 135.1 (s, C-4"), 131.8 (s, C-5), 130.2 (s, C-2", C-6"), 129.5 (s, C-2', CH), 128.9 (s, C-3", C-5"), 118.9 (s, C-3), 116.1 (s, C-10), 111.4 (s, C-6), 104.8 (s, C-8).

2b: IR (KBr): 3411 (br, OH), 3081, 2364 (Ar-CH), 1691 (C=O), 1457 (CH=CH), 1089 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.25 (d, 1H, CH), 7.19 (s, 2-H, CH), 6.37-7.89 (m, 7H, Ar-H), 4.92 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 190.1 (s, C-2', CO), 177.1 (s, C-4, C=O), 165.1 (s, C-7), 159.2 (s, C-9), 150.0 (s, C-2), 142.9 (s, C-1', CH), 141.0 (s, C-4", C-Cl), 135.8 (s, C-1"), 132.1 (s, C-2", C-6"), 131.8 (s, C-5), 130.1 (s, C-3", C-5"), 128.7 (s, C-2', CH), 120.1 (s, C-3), 117.4 (s, C-10), 110.1 (s, C-6), 106.4 (s, C-8).

2c: IR (KBr): 3381 (br, OH), 3085, 2366 (Ar-CH), 1686 (C=O), 1459 (CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.20 (s, 2-H, CH), 7.20 (d, 1H, CH), 6.38-7.74 (m, 7H, Ar-H), 5.01 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 188.8 (s, C-2', CO), 176.9 (s, C-4, C=O), 165.1 (s, C-7), 159.1 (s, C-9), 148.5 (s, C-2), 143.6 (s, C-1', CH), 137.1 (s, C-1"), 132.8 (s, C-3", C-5"), 132.0 (s, C-2", C-6"), 131.5 (s, C-5), 129.0 (s, C-4", C-Br), 128.9 (s, C-2', CH), 119.1 (s, C-3), 116.0 (s, C-10), 110.1 (s, C-6), 104.9 (s, C-8).

2d: IR (KBr): 3412 (br, OH), 3083, 2364 (Ar-CH), 1684 (C=O), 1458 (CH=CH), 1094 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.21 (d, 1H, CH), 7.19 (s, 2-H, CH), 6.39-7.71 (m, 7H, Ar-H), 5.03 (s, 1H, OH), 2.31 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6): δ 188.6 (s, C-2', CO), 176.5 (s, C-4, C=O), 165.4 (s, C-7), 158.4 (s, C-9), 150.1 (s, C-2), 144.4 (s, C-1', CH), 143.8 (s, C-4", C-CH_3), 135.1 (s, C-1"), 132.4 (s, C-5), 129.4 (s, C-2", C-6"), 129.1 (s, C-2', CH), 129.0 (s, C-3", C-5"), 118.8 (s, C-3), 117.0 (s, C-10), 111.1 (s, C-6), 105.0 (s, C-8), 24.0 (s, CH_3 of C-4").

2e: IR (KBr): 3412 (br, OH), 3083, 2366 (Ar-CH), 1686 (C=O), 1464 (CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.26 (d, 1H, CH), 7.23 (s, 2-H, CH), 6.34-7.73 (m, 7H, Ar-H), 4.98 (s, 1H, OH), 3.73 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): δ 190.1 (s, C-2', CO), 176.6 (s, C-4, C=O), 166.1 (s, C-7), 165.7 (s, C-4", C-CH_3), 157.9 (s, C-9), 148.7 (s, C-2), 143.0 (s, C-1', CH), 132.4 (s, C-5), 131.0 (s, C-2", C-6"), 129.8 (s, C-1"), 128.7 (s, C-2', CH), 118.6 (s, C-3), 115.8 (s, C-10), 115.0 (s, C-3", C-5"), 111.0 (s, C-6), 106.1 (s, C-8), 56.1 (s, OCH_3 of C-4").

Table I — Characterization data of the compounds **2a-i**

Compds	R	m.p. (^OC)	Mol. Formula	Crystallization solvent	Mol. wt	Found (Calcd) %			Yield (%)
						C	H	N	
2a	H	221	$C_{18}H_{12}O_4$	Ethanol	292	73.93 (73.97	4.10 4.14	-- --)	60
2b	Cl (*p*)	218	$C_{18}H_{11}ClO_4$	Benzene	327	66.15 (66.17	3.35 3.39	-- --)	51
2c	Br (*p*)	230	$C_{18}H_{11}BrO_4$	Benzene	371	58.21 (58.24	2.96 2.99	-- --)	61
2d	CH_3 (*p*)	215	$C_{19}H_{14}O_4$	Ethanol	306	74.47 (74.50	4.57 4.61	-- --)	52
2e	OCH_3 (*p*)	218	$C_{19}H_{14}O_5$	Benzene	322	70.78 (70.80	4.30 4.38	-- --)	59
2f	Cl_2 (*o*, *p*)	205	$C_{18}H_{10}Cl_2O_4$	Ethanol	361	59.85 (59.86	2.75 2.79	-- --)	55
2g	Cl_2 (*m*, *p*)	209	$C_{18}H_{10}Cl_2O_4$	Ethanol	361	59.85 (59.86	2.75 2.79	-- --)	58
2h	NO_2 (*m*)	220	$C_{18}H_{11}NO_6$	Benzene	337	64.08 (64.10	3.25 3.29	4.13 4.15)	53
2i	NO_2 (*p*)	280	$C_{18}H_{11}NO_6$	Benzene	337	64.08 (64.10	3.25 3.29	4.13 4.15)	60

2f: IR (KBr): 3388 (br, OH), 3045, 2361 (Ar-CH), 1689 (C=O), 1460 (CH=CH), 1093 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.79 (d, 1H, CH), 7.21 (d, 1H, CH), 7.19 (s, 2-H, CH), 6.36-7.67 (m, 6H, Ar-H), 5.11 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 189.0 (s, C-2', CO), 177.1 (s, C-4, C=O), 165.1 (s, C-7), 159.1 (s, C-9), 149.0 (s, C-2), 142.8 (s, C-1', CH), 142.0 (s, C-4", C-Cl), 135.4 (s, C-2", C-Cl), 134.6 (s, C-1"), 132.1 (s, C-6"), 131.7 (s, C-5), 130.0 (s, C-3"), 128.4 (s, C-2', CH), 127.1 (s, C-5"), 120.0 (s, C-3), 117.0 (s, C-10), 109.6 (s, C-6), 104.8 (s, C-8).

2h: IR (KBr): 3445 (br, OH), 3081, 2366 (Ar-CH), 1688 (C=O), 1461 (CH=CH), 1098 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.80 (d, 1H, CH), 7.25 (d, 1H, CH), 7.24 (s, 2-H, CH), 6.35-8.78 (m, 7H, Ar-H), 4.87 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 189.1 (s, C-2', CO), 177.8 (s, C-4, C=O), 165.0 (s, C-7), 157.6 (s, C-9), 147.6 (s, C-2), 147.2 (s, C-3", C-NO_2), 143.2 (s, C-1', CH), 138.0 (s, C-1"), 135.4 (s, C-6"), 131.0 (s, C-5), 129.6 (s, C-5"), 129.4 (s, C-2', CH), 126.3 (s, C-4") 124.5 (s, C-2"), 119.8 (s, C-3), 116.0 (s, C-10), 110.1 (s, C-6), 105.1 (s, C-8).

General procedure for the preparation of 7-hydroxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones 3a-i

A mixture of 7-hydroxy-3-(3-aryl-3-oxoprop-1-enyl)-4*H*-chromen-4-ones (0.01 moles) **2**, phenyl hydrazine hydrochloride (0.01 moles) and DMF (10 mL) were refluxed for 18 hr in an oil-bath. The reaction-mixture was cooled and added to crushed ice, the solid obtained was filtered and washed with water, dried and recrystallised from DMF. The physical and analytical data of compounds are given in **Table II**. The spectral data of various **3a-i** are described below.

3a: IR (KBr): 3428 (br, OH), 2363 (Ar-CH), 1626 (CO), 1456 (C=N), 1098 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.45 (s, 2-H, CH), 6.36-7.50 (m, 13H, Ar-H), 6.34 (s, 4'-H, CH), 5.12 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 176.1 (s, C-4, C=O), 164.8 (s, C-7),

Table II — Characterization data of the compounds **3a-i**

Compds	R	m.p.* (^OC)	Mol. Formula	Mol. w t	Found (Calcd) % C	H	N	Yield (%)
3a	H	325	$C_{24}H_{16}N_2O_3$	380	75.75	4.20	7.32	55
					(75.78	4.24	7.36)	
3b	Cl (*p*)	282	$C_{24}H_{15}ClN_2O_3$	415	69.45	3.60	6.71	52
					(69.49	3.64	6.75)	
3c	Br (*p*)	290	$C_{24}H_{15}BrN_2O_3$	459	62.74	3.25	6.05	54
					(62.76	3.29	6.10)	
3d	CH_3 (*p*)	265	$C_{25}H_{18}N_2O_3$	394	76.10	4.55	7.06	50
					(76.13	4.60	7.10)	
3e	OCH_3 (*p*)	275	$C_{25}H_{18}N_2O_4$	410	73.13	4.40	6.80	45
					(73.16	4.42	6.83)	
3f	Cl_2 (*o*, *p*)	260	$C_{24}H_{14}Cl_2N_2O_3$	450	64.00	3.34	6.20	56
					(64.02	3.36	6.22)	
3g	Cl_2 (*m*, *p*)	261	$C_{24}H_{14}Cl_2N_2O_3$	450	64.00	3.34	6.20	60
					(64.02	3.36	6.22)	
3h	NO_2 (*m*)	230	$C_{24}H_{15}N_3O_5$	425	67.74	3.55	9.80	61
					(67.76	3.55	9.88)	
3i	NO_2 (*p*)	235	$C_{24}H_{15}N_3O_5$	425	67.74	3.55	9.80	55
					(67.76	3.55	9.88)	

*All compounds crystallized from DMF.

158.7 (s, C-2), 158.4 (s, C-9), 147.0 (s, C-3'), 144.1 (s, C-5'), 132.1 (s, C-5), 128.0-133.6 (s, aromatic 12C-atom), 119.1 (s, C-3), 115.8 (s, C-10), 110.0 (s, C-6), 106.0 (s, C-8), 102.1 (s, C-4', CH); EI-MS: *m*/*z* (%) 380 (M^+, 100), 303 (21), 227 (20), 219 (17), 161 (28), 77 (11).

3b: IR (KBr): 3300 (br, OH), 2360 (Ar-CH), 1684 (CO), 1451 (C=N), 1098 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.50 (s, 2-H, CH), 6.41 (s, 4'-H, CH), 6.37-7.49 (m, 12H, Ar-H), 4.90 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 174.9 (s, C-4, C=O), 165.4 (s, C-7), 160.1 (s, C-2), 159.0 (s, C-9), 146.8 (s, C-3'), 143.0 (s, C-5'), 131.4 (s, C-5), 128.1-135.1 (s, aromatic 12C-atom), 118.0 (s, C-3), 117.0 (s, C-10), 109.9 (s, C-6), 106.1 (s, C-8), 102.0 (s, C-4', CH); EI-MS: *m*/*z* (%) 415 (M^+, 100), 303 (45), 253 (27), 227 (20), 161 (23), 77 (19).

3c: IR (KBr): 3455 (br, OH), 2364 (Ar-CH), 1714 (CO), 1454 (C=N), 1054 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.46 (s, 2-H, CH), 6.42 (s, 4'-H, CH), 6.33-7.51 (m, 12H, Ar-H), 5.10 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 175.0 (s, C-4, C=O), 164.8 (s, C-7), 158.9 (s, C-2), 157.6 (s, C-9), 148.1 (s, C-3'), 144.0 (s, C-5'), 132.1 (s, C-5), 123.0-131.7 (s, aromatic 12C-atom), 117.7 (s, C-3), 116.0 (s, C-10), 109.9 (s, C-6), 105.0 (s, C-8), 102.8 (s, C-4', CH); EI-MS: *m*/*z* (%) 459 (M^+, 100), 303 (31), 297 (21), 227 (21), 161 (19), 77 (32).

3d: IR (KBr): 3411 (br, OH), 2364 (Ar-CH), 1700 (CO), 1461 (C=N), 1074 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.50 (s, 2-H, CH), 6.41 (s, 4'-H, CH), 6.32-7.49 (m, 12H, Ar-H), 5.01 (s, 1H, OH), 2.27 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6): 174.7 (s, C-4, C=O), 164.8 (s, C-7), 159.1 (s, C-9), 159.0 (s, C-2), 146.8 (s, C-3'), 142.7 (s, C-5'), 131.7 (s, C-5), 126.7-138.0 (s, aromatic 12C-atom), 118.8 (s, C-3), 116.9 (s, C-10), 109.8 (s, C-6), 105.1 (s, C-8), 102.4 (s, C-4', CH), 23.4 (s, CH_3); EI-MS: *m*/*z* (%) 394 (M^+, 100), 303 (21), 233 (26), 227 (19), 161 (35), 77 (24).

3e: IR (KBr): 3443 (br, OH), 2361 (Ar-CH), 1701 (CO), 1458 (C=N), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.48 (s, 2-H, CH), 6.38 (s, 4'-H, CH), 6.35-7.51 (m, 12H, Ar-H), 4.87 (s, 1H, OH), 3.69 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): 174.7 (s, C-4, C=O), 164.5 (s, C-7), 158.6 (s, C-2), 158.0 (s, C-9), 146.1 (s, C-3'), 143.1 (s, C-5'), 131.5 (s, C-5), 117.6 (s, C-3), 117.2 (s, C-10), 115.1-161.1 (s, aromatic 12C-atom), 109.9 (s, C-6), 105.0 (s, C-8), 102.1 (s, C-4', CH), 56.2 (s, OCH_3).

3f: IR (KBr): 3391 (br, OH), 2364 (Ar-CH), 1713 (CO), 1451 (C=N), 1055 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.51 (s, 2-H, CH), 6.38 (s, 4'-H, CH), 6.39-7.51 (m, 11H, Ar-H), 5.03 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 174.6 (s, C-4, C=O), 164.3 (s, C-7), 159.1 (s, C-2), 159.0 (s, C-9), 146.9 (s, C-3'), 143.2 (s, C-5'), 131.8 (s, C-5), 127.0-135.2 (s, aromatic 12C-atom), 118.0 (s, C-3), 116.1 (s, C-10), 111.1 (s, C-6), 104.8 (s, C-8), 101.7 (s, C-4', CH); EI-MS: *m*/*z* (%) 450 (M^+, 100), 303 (42), 288 (31), 227 (24), 161 (36), 77 (28).

3h: IR (KBr): 3389 (br, OH), 2360 (Ar-CH), 1710 (CO), 1451 (C=N), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.47 (s, 2-H, CH), 6.38 (s, 4'-H, CH), 6.41-8.45 (m, 12H, Ar-H), 4.94 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 176.2 (s, C-4, C=O), 165.4 (s, C-7), 159.4 (s, C-2), 158.1 (s, C-9), 146.9 (s, C-3'), 144.0 (s, C-5'), 131.6 (s, C-5), 120.6-149.2 (s, aromatic 12C-atom), 117.5 (s, C-3), 117.1 (s, C-10), 111.1 (s, C-6), 104.8 (s, C-8), 102.1 (s, C-4', CH).

General procedure for the preparation of 2, 3, 4, 6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones 4a-i

A mixture of 7-hydroxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones (0.39 mmole) **3**, K_2CO_3 (0.43 mmole) and acetonitrile (40 mL) was stirred at room temp. for 2 hr under argon atmosphere. 18-Crown-6 (0.04 mmoles) was added followed by α-acetobromoglucose (0.58 mmoles). After 5 hr, it was poured on to ice-cold water and neutralized with H_2SO_4 (1mole/L). The product was extracted in ethyl acetate (50mL × 4). The extract was concentrated under reduce pressure to afford a brown coloured semi-solid. The physical and analytical data of compounds are given in **Table III**. The spectral data of various **4a-i** are described below.

4a: IR (KBr): 3042, 2361 (Ar-CH), 2854 (glucosidic-CH), 1760 (C=O of *O*-acetyl gps of glycone moiety), 1626 (C=O), 1454 (C=N), 1027 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.46 (s, 2-H, CH), 6.44 (s, 4'-H, CH), 6.42-7.55 (m, 13H, Ar-H), 4.84-5.05 (m, 3H, 2", 3", 4"-H), 4.86 (d, 1H, 1"-H, anomeric proton), 4.34 (dd, 1H, 5"-H), 3.80-4.29 (m, 2H, 6"-H), 2.01, 1.95, 1.99, 2.05 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 176.0 (s, C-4, C=O), 169.6 (s, C-atoms of acetyl C=O), 163.9 (s, C-7), 158.9 (s, C-2), 157.4 (s, C-9), 147.2 (s, C-3'), 143.4 (s, C-5'), 130.8 (s, C-5), 127.1-133.6 (s, aromatic 12C-atom), 118.1 (s, C-3), 115.5 (s, C-10), 108.9 (s, C-6), 103.4 (s, C-8), 102.1 (s, C-4', CH), 101.8 (s, C-1", anomeric C-atom), 74.8 (s, C-5"), 72.1 (s, C-2"), 70.8 (s, C-4"),

Table III — Characterization data of the compounds **4a-i***

Compds	R	Mol. Formula	$[\alpha]_D^{25}$ (°)	Mol. wt	Found (Calcd) % C	H	N	Yield (%)
4a	H	$C_{38}H_{34}N_2O_{12}$	-24.2	711	64.20 (64.22	4.80 4.82	3.90 3.94)	74
4b	Cl (*p*)	$C_{38}H_{33}ClN_2O_{12}$	-30.4	745	61.20 (61.25	4.40 4.46	3.71 3.76)	70
4c	Br (*p*)	$C_{38}H_{33}BrN_2O_{12}$	-31.1	790	51.74 (51.80	4.14 4.21	3.50 3.55)	65
4d	CH_3 (*p*)	$C_{39}H_{36}N_2O_{12}$	-25.4	725	64.60 (64.64	5.00 5.01	3.85 3.87)	69
4e	OCH_3 (*p*)	$C_{39}H_{36}N_2O_{13}$	-32.9	745	63.20 (63.24	4.90 4.90	3.70 3.78)	73
4f	Cl_2 (*o*, *p*)	$C_{38}H_{32}Cl_2N_2O_{12}$	-29.0	780	58.50 (58.55	4.05 4.14	3.50 3.59)	75
4g	Cl_2 (*m*, *p*)	$C_{38}H_{32}Cl_2N_2O_{12}$	-28.3	780	58.50 (58.55	4.05 4.14	3.50 3.59)	70
4h	NO_2 (*m*)	$C_{38}H_{33}N_2O_{14}$	-27.6	756	60.35 (60.40	4.35 4.40	5.51 5.56)	68
4i	NO_2 (*p*)	$C_{38}H_{33}N_2O_{14}$	-29.6	756	60.35 (60.40	4.35 4.40	5.51 5.56)	76

*Majority of the compounds are syrupy in nature

70.5 (s, C-3"), 64.9 (s, C-6"), 20.4 (s, C-atom, CH_3 of acetyl group).

4b: IR (KBr): 3044, 2365 (Ar-CH), 2857 (glucosidic-CH), 1754 (C=O of *O*-acetyl gps of glycone moiety), 1722 (C=O), 1451 (C=N), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.54 (s, 2-H, CH), 6.37 (s, 4'-H, CH), 6.42-7.59 (m, 12H, Ar-H), 4.75-4.99 (m, 3H, 2", 3", 4"-H), 4.79 (d, 1H, 1"-H, anomeric proton), 4.34 (dd, 1H, 5"-H), 3.98-4.32 (m, 2H, 6"-H), 2.02, 1.96, 1.94, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 176.1 (s, C-4, C=O), 170.3 (s, C-atoms of acetyl C=O), 164.2 (s, C-7), 159.0 (s, C-2), 157.6 (s, C-9), 147.4 (s, C-3'), 143.1 (s, C-5'), 130.8 (s, C-5), 128.5-134.9 (s, aromatic 12C-atom), 119.0 (s, C-3), 116.1(s, C-10), 109.0 (s, C-6), 103.6 (s, C-8), 102.6 (s, C-4', CH), 102.4 (s, C-1", anomeric C-atom), 75.2 (s, C-5"), 72.2 (s, C-2"), 71.4 (s, C-4"), 71.0 (s, C-3"), 66.1(s, C-6"), 20.5 (s, C-atom, CH_3 of acetyl group).

4c: IR (KBr): 3040, 2361 (Ar-CH), 2852 (glucosidic-CH), 1765 (C=O of *O*-acetyl gps of glycone moiety), 1724 (C=O), 1452 (C=N), 1048 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.46 (s, 2-H, CH), 6.39 (s, 4'-H, CH), 6.44-7.56 (m, 12H, Ar-H), 4.78-5.05 (m, 3H, 2", 3", 4"-H), 4.78 (d, 1H, 1"-H, anomeric proton), 4.41 (dd, 1H, 5"-H), 3.89-4.29 (m, 2H, 6"-H), 1.99, 1.94, 1.98, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 176.0 (s, C-4, C=O), 170.0 (s, C-atoms of acetyl C=O), 163.8 (s, C-7), 158.9 (s, C-2), 158.1 (s, C-9), 148.2 (s, C-3'), 143.1 (s, C-5'), 131.0 (s, C-5), 123.5-132.9 (s, aromatic 12C-atom), 118.1 (s, C-3), 115.0 (s, C-10), 108.9 (s, C-6), 103.4 (s, C-8), 102.5 (s, C-4', CH), 102.5 (s, C-1", anomeric C-atom), 75.4 (s, C-5"), 72.3 (s, C-2"), 71.0 (s, C-4"), 70.9 (s, C-3"), 66.1 (s, C-6"), 21.1 (s, C-atom, CH_3 of acetyl group).

4d: IR (KBr): 3041, 2362 (Ar-CH), 2856 (glucosidic-CH), 1761 (C=O of *O*-acetyl gps of glycone moiety), 1726 (C=O), 1454 (C=N), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.44 (s, 2-H, CH), 6.34 (s, 4'-H, CH), 6.41-7.58 (m, 12H, Ar-H), 4.72-5.11 (m, 3H, 2", 3", 4"-H), 4.89 (d, 1H, 1"-H, anomeric proton), 4.49 (dd, 1H, 5"-H), 3.75-4.29 (m, 2H, 6"-H), 2.37 (s, 3H, CH_3), 2.02, 1.94, 1.98, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 176.0 (s, C-4, C=O), 170.6 (s, C-atoms of acetyl C=O), 164.7 (s, C-7), 159.0 (s, C-2), 157.4 (s, C-9), 147.4 (s, C-3'), 143.1 (s, C-5'), 130.6 (s, C-5), 127.1-138.9 (s, aromatic 12C-atom), 118.1 (s, C-3), 115.0 (s, C-10), 108.8 (s, C-6), 103.4 (s, C-8), 102.0 (s, C-4', CH), 102.6 (s, C-1", anomeric C-atom), 75.4 (s, C-5"), 72.1 (s, C-2"), 71.1 (s, C-4"), 71.0 (s, C-3"), 65.7 (s, C-6"), 23.7 (s, C-atom, CH_3), 20.7 (s, C-atom, CH_3 of acetyl group).

4e: IR (KBr): 3037, 2367 (Ar-CH), 2861 (glucosidic-CH), 1754 (C=O of *O*-acetyl gps of glycone moiety), 1727 (C=O), 1460 (C=N), 1100 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.45 (s, 2-H, CH), 6.33 (s, 4'-H, CH), 6.39-7.61 (m, 12H, Ar-H), 4.89 (d, 1H, 1"-H, anomeric proton), 4.71-5.05 (m, 3H, 2", 3",

4"-H), 4.48 (dd, 1H, 5"-H), 3.74-4.29 (m, 2H, 6"-H), 3.65 (s, 3H, OCH_3), 1.97, 1.98, 1.97, 2.00 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 174.8 (s, C-4, C=O), 170.4 (s, C-atoms of acetyl C=O), 163.9 (s, C-7), 159.0 (s, C-2), 157.4 (s, C-9), 147.4 (s, C-3'), 143.1 (s, C-5'), 130.7 (s, C-5), 113.5-161.5 (s, aromatic 12C-atom), 119.1 (s, C-3), 115.0 (s, C-10), 108.7 (s, C-6), 103.4 (s, C-8), 102.0 (s, C-4', CH), 101.7 (s, C-1", anomeric C-atom), 74.7 (s, C-5"), 72.1 (s, C-2"), 70.9 (s, C-4"), 70.4 (s, C-3"), 66.1 (s, C-6"), 56.2 (s, C-atom, OCH_3), 20.7 (s, C-atom, CH_3 of acetyl group).

4f: IR (KBr): 3045, 2360 (Ar-CH), 2851 (glucosidic-CH), 1761 (C=O of *O*-acetyl gps of glycone moiety), 1700 (C=O), 1457 (C=N), 1077 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.48 (s, 2-H, CH), 6.38 (s, 4'-H, CH), 6.35-7.64 (m, 11H, Ar-H), 4.78-4.99 (m, 3H, 2", 3", 4"-H), 4.79 (d, 1H, 1"-H, anomeric proton), 4.44 (dd, 1H, 5"-H), 3.78-4.27 (m, 2H, 6"-H), 1.97, 1.98, 1.99, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 174.8 (s, C-4, C=O), 171.0 (s, C-atoms of acetyl C=O), 163.8 (s, C-7), 159.7 (s, C-2), 158.1 (s, C-9), 147.5 (s, C-3'), 143.2 (s, C-5'), 130.8 (s, C-5), 126.8-135.9 (s, aromatic 12C-atom), 117.9 (s, C-3), 115.0 (s, C-10), 108.7 (s, C-6), 103.4 (s, C-8), 102.0 (s, C-4', CH), 101.7 (s, C-1", anomeric C-atom), 75.4 (s, C-5"), 72.1 (s, C-2"), 71.7 (s, C-4"), 71.4 (s, C-3"), 66.4 (s, C-6"), 21.8 (s, C-atom, CH_3 of acetyl group).

4h: IR (KBr): 3044, 2360 (Ar-CH), 2851 (glucosidic-CH), 1764 (C=O of *O*-acetyl gps of glycone moiety), 1708 (C=O), 1457 (C=N), 1048 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.49 (s, 2-H, CH), 6.47 (s, 4'-H, CH), 6.40-8.45 (m, 12H, Ar-H), 4.78-5.01 (m, 3H, 2", 3", 4"-H), 4.81 (d, 1H, 1"-H, anomeric proton), 4.40 (dd, 1H, 5"-H), 3.78-4.29 (m, 2H, 6"-H), 1.98, 1.97, 1.99, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): 174.7 (s, C-4, C=O), 170.0 (s, C-atoms of acetyl C=O), 163.7 (s, C-7), 158.7 (s, C-2), 157.4 (s, C-9), 147.2 (s, C-3'), 143.0 (s, C-5'), 130.8 (s, C-5), 121.5-149.4 (s, aromatic 12C-atom), 117.5 (s, C-3), 114.8 (s, C-10), 108.6 (s, C-6), 103.4 (s, C-8), 102.3 (s, C-4', CH), 101.7 (s, C-1", anomeric C-atom), 75.4 (s, C-5"), 72.1 (s, C-2"), 71.1 (s, C-4"), 70.8 (s, C-3"), 65.1 (s, C-6"), 21.8 (s, C-atom, CH_3 of acetyl group).

General procedure for the preparation of 7-*O*-β-D-glucopyranosyl-oxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones 5a-i

The mixture of 2, 3, 4, 6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(1-phenyl-3-aryl-1*H*-pyrazol-5-yl)-4*H*-chromen-4-ones **4** (0.109 mmoles), absolute methanol (2 mL) and anhydrous zinc acetate (0.126 mmoles) was refluxed for 7 hr. After cooled down at room temp., 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 the brown coloured semisolid. The physical and analytical data of compounds are given in **Table IV**. The spectral data of various **5a-i** are described below.

5a: IR (KBr): 3401 (br, OH peak of carbohydrate residue), 2853 (glucosidic-CH), 2899, 2364 (Ar-CH), 1720 (C=O), 1405 (C=N), 1032 (C-O-C), 683 cm^{-1} (benzene monosubstituted); ^{1}H NMR (DMSO-d_6): δ 7.47 (s, 2-H, CH), 6.44 (s, 4'-H, CH), 6.40-7.57 (m, 13H, Ar-H), 5.77 (d, 1"-H, 1H, anomeric proton), 3.47-3.99 (m, 3H, 2", 3", 4"-H), 3.71 (dd, 1H, 5"-H), 3.49-3.87 (m, 2H, 6"-H); ^{13}C NMR (DMSO-d_6): 176.0 (s, C-4, C=O), 163.7 (s, C-7), 160.1 (s, C-2), 158.2 (s, C-9), 146.9 (s, C-3'), 143.1 (s, C-5'), 130.7 (s, C-5), 127.0-133.8 (s, aromatic 12C-atom), 118.1 (s, C-3), 116.3 (s, C-10), 109.5 (s, C-6), 104.7 (s, C-1", anomeric C-atom), 104.5 (s, C-8), 101.9 (s, C-4', CH), 81.1 (s, C-5"), 77.3 (s, C-3"), 75.7 (s, C-2"), 73.0 (s, C-4"), 66.4 (s, C-6"); EI-MS: *m*/*z* (%) 544 ([M+1]$^+$, 19), 381 (100), 303 (35), 227 (27), 219 (19), 163 (39), 161 (25), 77 (24).

5b: IR (KBr): 3424 (br, OH peak of carbohydrate residue), 2845 (glucosidic-CH), 2360 (Ar-CH), 1712 (C=O), 1455 (C=N), 1089 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.27 (s, 2-H, CH), 6.39 (s, 4'-H, CH), 6.39-7.60 (m, 12H, Ar-H), 5.75 (d, 1H, 1"-H, anomeric proton), 3.45-3.94 (m, 3H, 2", 3", 4"-H), 3.88 (dd, 1H, 5"-H), 3.44-3.91 (m, 2H, 6"-H); ^{13}C NMR (DMSO-d_6): 175.7 (s, C-4, C=O), 163.5 (s, C-7), 159.8 (s, C-2), 158.2 (s, C-9), 147.0 (s, C-3'), 142.9 (s, C-5'), 130.4 (s, C-5), 128.0-134.9 (s, aromatic 12C-atom), 117.8 (s, C-3), 115.1 (s, C-10), 108.7 (s, C-6), 106.1 (s, C-1", anomeric C-atom), 104.5 (s, C-8), 103.6 (s, C-4', CH), 82.0 (s, C-5"), 77.0 (s, C-3"), 75.2 (s, C-2"), 73.1 (s, C-4"), 64.8 (s, C-6"); EI-MS: *m*/*z* (%) 578 ([M+1]$^+$, 16), 415 (100), 303 (27), 253 (35), 227 (39), 163 (41), 161 (28), 77 (21).

5c: IR (KBr): 3399 (br, OH peak of carbohydrate residue), 2844 (glucosidic-CH), 2363 (Ar-CH), 1729 (C=O), 1444 (C=N), 1091 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.49 (s, 2-H, CH), 6.38 (s, 4'-H, CH), 6.40-7.58 (m, 12H, Ar-H), 3.48-3.98 (m, 3H, 2", 3", 4"-H), 5.68 (d, 1H, 1"-H, anomeric proton), 3.84 (dd, 1H, 5"-H), 3.50-3.86 (m, 2H, 6"-H); ^{13}C NMR (DMSO-d_6): 175.1 (s, C-4, C=O), 163.8 (s, C-7),

Table IV — Characterization data of the compounds **5a-i***

Compds	R	Mol. Formula	$[\alpha]_D^{25}$ (°)	Mol. wt	Found (Calcd) % C	H	N	Yield (%)
5a	H	$C_{30}H_{26}N_2O_8$	- 14.1	543	66.39 (66.42)	4.74 4.82	5.10 5.16)	90
5b	Cl (*p*)	$C_{30}H_{25}ClN_2O_8$	- 13.4	577	62.40 (62.45	4.30 4.36	4.81 4.86)	89
5c	Br (*p*)	$C_{30}H_{25}BrN_2O_8$	- 16.7	621	57.90 (57.98	4.01 4.05	4.46 4.51)	75
5d	CH_3 (*p*)	$C_{31}H_{28}N_2O_8$	- 13.1	557	66.85 (66.90	5.04 5.06	5.01 5.03)	81
5e	OCH_3 (*p*)	$C_{31}H_{28}N_2O_9$	- 18.4	573	65.01 (65.03	4.90 4.92	4.85 4.89)	69
5f	Cl_2 (*o*, *p*)	$C_{30}H_{24}Cl_2N_2O_8$	- 19.9	611	58.90 (58.93	3.84 3.95	4.50 4.58)	87
5g	Cl_2 (*m*, *p*)	$C_{30}H_{24}Cl_2N_2O_8$	- 16.7	611	58.90 (58.93	3.90 3.95	4.55 4.58)	82
5h	NO_2 (*m*)	$C_{30}H_{25}N_3O_{10}$	- 17.3	588	61.30 (61.33	4.25 4.28	7.10 7.15)	79
5i	NO_2 (*p*)	$C_{30}H_{25}N_3O_{10}$	- 14.6	588	61.30 (61.33	4.25 4.28	7.15 7.15)	80

*All the compounds are syrupy in nature

158.9 (s, C-2), 158.1 (s, C-9), 148.2 (s, C-3'), 144.2 (s, C-5'), 130.8 (s, C-5), 123.0-132.5 (s, aromatic 12C-atom), 117.6 (s, C-3), 114.8 (s, C-10), 109.8 (s, C-6), 106.2 (s, C-1", anomeric C-atom), 103.0 (s, C-8), 102.0 (s, C-4', CH), 82.2 (s, C-5"), 77.0 (s, C-3"), 75.0 (s, C-2"), 73.1 (s, C-4"), 64.6 (s, C-6"); EI-MS: *m*/*z* (%) 622 ($[M+1]^+$, 25), 459 (100), 303 (18), 297 (20), 227 (29), 163 (35), 161 (31), 77 (17).

5d: IR (KBr): 3424 (br, OH peak of carbohydrate residue), 2858 (glucosidic-CH), 2360 (Ar-CH), 1727 (C=O), 1459 (C=N), 1089 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.51 (s, 2-H, CH), 6.44 (s, 4'-H, CH), 6.40-7.60 (m, 12H, Ar-H), 5.68 (d, 1H, 1"-H, anomeric proton), 3.49-3.97 (m, 3H, 2", 3", 4"-H), 3.88 (dd, 1H, 5"-H), 3.59-3.89 (m, 2H, 6"-H), 2.29 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6): 174.7 (s, C-4, C=O), 163.6 (s, C-7), 159.6 (s, C-2), 158.2 (s, C-9), 146.4 (s, C-3'), 143.0 (s, C-5'), 130.4 (s, C-5), 127.5-138.9 (s, aromatic 12C-atom), 118.0 (s, C-3), 115.1 (s, C-10), 108.8 (s, C-6), 104.9 (s, C-1", anomeric C-atom), 104.3 (s, C-8), 103.1 (s, C-4', CH), 81.1 (s, C-5"), 77.8 (s, C-3"), 75.0 (s, C-2"), 73.1 (s, C-4"), 66.0 (s, C-6"), 23.7 (s, C-atom, CH_3); EI-MS: *m*/*z* (%) 557 (M^+, 19), 394 (100), 303 (24), 233 (41), 227 (36), 163 (30), 161 (11), 77 (18).

5e: IR (KBr): 3419 (br, OH peak of carbohydrate residue), 2849 (glucosidic-CH), 2362 (Ar-CH), 1700 (C=O), 1455 (C=N), 1092 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.45 (s, 2-H, CH), 6.41 (s, 4'-H, CH), 6.41-7.59 (m, 12H, Ar-H), 5.75 (d, 1H, 1"-H, anomeric proton), 3.35-3.92 (m, 3H, 2", 3", 4"-H), 3.90 (dd, 1H, 5"-H), 3.45-3.84 (m, 2H, 6"-H), 3.79 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): 176.1 (s, C-4, C=O), 163.8 (s, C-7), 158.9 (s, C-2), 158.2 (s, C-9), 148.1 (s, C-3'), 143.1 (s, C-5'), 132.4 (s, C-5), 115.0-161.5 (s, aromatic 12C-atom), 117.6 (s, C-3), 115.0 (s, C-10), 109.8 (s, C-6), 104.8 (s, C-1", anomeric C-atom), 103.2 (s, C-8), 102.3 (s, C-4', CH), 81.4 (s, C-5"), 77.2 (s, C-3"), 75.2 (s, C-2"), 73.1 (s, C-4"), 64.8 (s, C-6"), 56.1 (s, C-atom, OCH_3).

5f: IR (KBr): 3421 (br, OH peak of carbohydrate residue), 2851 (glucosidic-CH), 2364 (Ar-CH), 1701 (C=O), 1445 (C=N), 1073 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.48 (s, 2-H, CH), 6.39 (s, 4'-H, CH), 6.39-7.58 (m, 11H, Ar-H), 3.39-3.90 (m, 3H, 2", 3", 4"-H), 5.71 (d, 1H, 1"-H, anomeric proton), 3.79 (dd, 1H, 5"-H), 3.47-3.94 (m, 2H, 6"-H); ^{13}C NMR (DMSO-d_6): 175.8 (s, C-4, C=O), 164.1 (s, C-7), 159.6 (s, C-2), 158.1 (s, C-9), 148.3 (s, C-3'), 144.2 (s, C-5'), 131.4 (s, C-5), 127.5-135.9 (s, aromatic 12C-atom), 117.9 (s, C-3), 115.1 (s, C-10), 108.4 (s, C-6), 104.0 (s, C-1", anomeric C-atom), 103.4 (s, C-8), 102.1 (s, C-4', CH), 81.2 (s, C-5"), 77.2 (s, C-3"), 75.3 (s, C-2"), 73.2 (s, C-4"), 64.7 (s, C-6"); EI-MS: *m*/*z* (%) 612 ($[M+1]^+$, 22), 450 (100), 303 (31), 288 (15), 227 (28), 163 (37), 161 (31), 77 (26).

Table V — Antimicrobial and anti-oxidant activity of compounds **3a-i** and **5a-i**

Sr. No.	Zone of Inhibition (mm) (Activity Index) [std]						% Inhibition Antioxidant activity
	Antibacterial Activity				Antifungal Activity		
	Gram-positive		Gram-negative				
	S. aureus	*B. substilis*	*E. coli*	*K. aerogens*	*C. albicans*	*A. niger*	DPPH
3a	20(0.58)* (0.65)#	17(0.59)* (0.65)#	17 (0.49)* (0.59)#	22 (1.00)* (1.04)#	30 (1.43)* (1.30)#	19 (0.76)* (0.79)#	86.56 (0.88)*
3b	21(0.62)* (0.68)#	19 (0.66)* (0.73)#	19 (0.54)* (0.66)#	19 (0.86)* (0.90)#	27 (1.29)* (1.17)#	20 (0.80)* (0.83)#	88.73 (0.90)*
3c	20(0.58)* (0.65)#	19 (0.66)* (0.73)#	22 (0.63)* (0.76)#	20 (0.91)* (0.95)#	23 (1.09)* (1.00)#	16 (0.64)* (0.66)#	86.10 (0.86)*
3d	21(0.62)* (0.68)#	18 (0.62)* (0.69)#	17 (0.49)* (0.59)#	17 (0.77)* (0.81)#	23 (1.09)* (1.00)#	18(0.72)* (0.75)#	79.87 (0.81)*
3e	24 (0.71)* (0.77)#	20 (0.69)* (0.77)#	20 (0.57)* (0.69)#	19 (0.86)* (0.90)#	25 (1.19)* (1.07)#	20 (0.80)* (0.83)#	80.56 (0.87)*
3f	23 (0.68)* (0.74)#	17(0.59)* (0.65)#	21 (0.60)* (0.72)#	24 (1.09)* (1.14)#	23 (1.09)* (1.00)#	22 (0.88)* (0.92)#	86.13 (0.86)*
3g	23 (0.68)* (0.74)#	22 (0.76)* (0.85)#	20 (0.57)* (0.69)#	22 (1.00)* (1.04)#	29 (1.38)* (1.26)#	19 (0.76)* (0.79)#	85.56 (0.87)*
3h	22(0.65)* (0.71)#	18 (0.62)* (0.69)#	16 (0.46)* (0.55)#	17 (0.77)* (0.81)#	19 (0.90)* (0.83)#	16 (0.64)* (0.66)#	88.75 (0.90)*
3i	25(0.74)* (0.81)#	20 (0.69)* (0.77)#	21 (0.60)* (0.72)#	19 (0.86)* (0.90)#	20 (0.95)* (0.87)#	20 (0.80)* (0.83)#	86.45 (0.88)*
5a	28(0.82)* (0.90)#	20 (0.69)* (0.77)#	18 (0.51)* (0.62)#	24 (1.09)* (1.14)#	34(1.62)* (1.48)#	21(0.84)* (0.88)#	88.68 (0.90)*
5b	26(0.76)* (0.84)#	18 (0.62)* (0.69)#	20 (0.57)* (0.69)#	20 (0.91)* (0.95)#	29(1.38)* (1.26)#	21(0.84)* (0.88)#	90.76 (0.93)*
5c	22(0.65)* (0.71)#	22 (0.76)* (0.85)#	24 (0.69)* (0.83)#	22 (1.00)* (1.04)#	22(1.04)* (0.96)#	18(0.72)* (0.75)#	87.19 (0.89)*
5d	25(0.74)* (0.81)#	21(0.72)* (0.81)#	18 (0.51)* (0.62)#	19 (0.86)* (0.90)#	25(1.19)* (1.09)#	19 (0.76)* (0.79)#	80.57 (0.82)*
5e	31 (0.91)* (1.00)#	24 (0.83)* (0.92)#	22 (0.63)* (0.76)#	22 (1.00)* (1.04)#	27 (1.29)* (1.17)#	22 (0.88)* (0.92)#	82.45 (0.84)*
5f	33 (0.97)* (1.06)#	22 (0.76)* (0.85)#	20 (0.57)* (0.69)#	27 (1.23)* (1.29)#	25 (1.19)* (1.07)#	23 (0.92)* (0.96)#	88.73 (0.90)*
5g	30 (0.88)* (0.97)#	27 (0.93)* (1.04)#	19 (0.54)* (0.66)#	24 (1.09)* (1.14)#	30 (1.43)* (1.30)#	22 (0.88)* (0.92)#	86.12 (0.88)*
5h	25 (0.74)* (0.81)#	19 (0.66)* (0.73)#	17 (0.49)* (0.59)#	17 (0.77)* (0.81)#	20 (0.95)* (0.87)#	16 (0.64)* (0.66)#	91.65 (0.93)*
5i	31 (0.91)* (1.00)#	23 (0.79)* (0.88)#	23 (0.66)* (0.79)#	20 (0.91)* (0.95)#	23 (1.09)* (1.00)#	21 (0.84)* (0.88)#	86.56 (0.88)*
Std.1	34	29	35	22	21	25	98.03
Std. 2	31	26	29	21	23	24	

(Activity index) = Inhibition zone of the sample / Inhibition zone of the standard
* = Activity index against std. 1
# = Activity index against std. 2
For antibacterial activity: Std. 1 = ciprofloxacin and Std. 2 = sulphacetamide, For antifungal activity: Std. 1 = gentamycin and Std. 2 = clotrimazole. For anti-oxidant activity: Std. 1= ascorbic Acid.

5h: IR (KBr): 3424 (br, OH peak of carbohydrate residue), 2851 (glucosidic-CH), 2361 (Ar-CH), 1711 (C=O), 1449 (C=N), 1089 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.47 (s, 2-H, CH), 6.55 (s, 4'-H, CH), 6.48-8.49 (m, 12H, Ar-H), 5.77 (d, 1H, 1"-H, anomeric proton), 3.38-3.99 (m, 3H, 2", 3", 4"-H), 3.89 (dd, 1H, 5"-H), 3.38-3.75 (m, 2H, 6"-H); ^{13}C NMR (DMSO-d_6): 174.8 (s, C-4, C=O), 163.8 (s, C-7), 158.6 (s, C-2), 158.0 (s, C-9), 148.1 (s, C-3'), 142.9 (s, C-5'), 130.8 (s, C-5), 120.5-149.5 (s, aromatic 12C-atom), 118.0 (s, C-3), 116.4 (s, C-10), 109.6 (s, C-6), 106.0 (s, C-1", anomeric C-atom), 104.1 (s, C-8), 102.0 (s, C-4', CH), 82.1 (s, C-5"), 77.3 (s, C-3"), 75.2 (s, C-2"), 73.0 (s, C-4"), 64.8 (s, C-6"); EI-MS: *m*/*z* (%) 589 ($[M+1]^+$, 23), 426 (100), 303 (31), 227 (35), 163 (47), 161 (21), 77 (18).

The results of antimicrobial (antibacterial and antifungal) activity and anti-oxidant activity were shown in **Table V**.

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