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Synthesis of Some Peracetylated Glucopyranosyl Thiosemicarbazones of Substituted 4-Formylcoumarins

NGUYEN DINH THANH* and VU NGOC TOAN

Faculty of Chemistry, College of Science, Hanoi National University, 19 Le Thanh Tong, Hanoi 10000, Vietnam

*Corresponding author: Fax: +84 4 38241140; Tel: +84 4 38261853; E-mail: nguyendinhthanh@hus.edu.vn

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Some substituted 4-formylcoumarins were prepared by oxidation of 4-corresponding formylcoumarins using SeO_2. These aldehydes were converted to thiosemicarbazones by condensation reaction with tetra-*O*-acetyl-β-D-glucopyranosyl thiosemicarbazide usingmicrowave-assisted heating method. The synthesized compounds were characterized by FT-IR and ^{1}H NMR, ^{13}C NMR and mass spectral studies.

Key Words: Thiosemicarbazide, Glucopyranose, Thiosemicarbazones, Microwave-assisted, 4-Formylcoumarin.

INTRODUCTION

Coumarin derivatives have been used widely for the treatment of a numberous diseases such as heart disease[1-3], lymphoedema and other high-protein edemas[4]. They have also found pharmaceutical applications in the treatment of patients with chronic venous insufficiency[5], skin cancer[6], renal cell carcinoma[7], prostate cancer[8] as well as in the treatment of thermal injuries[9]. They may also be useful in preventing oxidative stress and apoptosis in HIV infection[10].

Thiosemicarbazides exhibit various biological activities and are extensively applied in medicine, particularly in the treatment of tuberculosis[11,12]. Numerous compounds with a thiosemicarbazone moiety also exhibit biological activity[13,14]. Several peracetylated glycopyranosyl thiosemicarbazones were synthesized[15,16]. Some peracetylated glycopyranosyl thiosemicarbazones containing coumarin ring were synthesized in good yields by the reactions of substituted 3-acetylcoumarins with 4-(tetra-*O*-acetyl-β-D-glucopyranosyl) thiosemicarbazide in our lab[17]. Continuing our works on glycopyranosyl thiosemicarbazones[18-20], we reported herein the synthesis of some substituted 4-formylcoumarin 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones.

EXPERIMENTAL

All solvents and reagents were purchased from Merck (Vietnam). Melting points were determined by open capillary method on STUART SMP3 instrument (BIBBY STERILIN-UK) and are uncorrected. IR spectra (KBr disc) were recorded on a Impact 410 FT-IR Spectrometer (Nicolet, USA). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance spectrometer AV500 (Bruker, Germany) at 500.13 MHz and 125.77 MHz, respectively, using DMSO-d_6 as solvent and TMS as an internal standard. MS spectra were recorded on mass spectrometer LTQ Orbitrap XL™ (Thermo Scientific, USA) using ESI method. All the starting benzaldehydes were purchased from commercial suppliers (Merck-Germany) and used with no further purification. All other solvents and reagents were used as received or purified by standard protocols. 4-(Tetra-*O*-acetyl-β-glucopyranosyl)thiosemicarbazide were prepared from tetra-*O*-acetyl-β-glucopyranosyl isothiocyanate[16]. 4-Formyl-6-(or 7-)-methyl/alkoxy-4-formylcoumarins were synthesized based on the synthetic method for 4-formyl-7-methoxylcoumarin[21].

Synthesis of thiosemicarbazones (4a-f): To a solution of 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazide (1 mmol) in 99 % ethanol (10 mL) substituted 4-formylcoumarin 3 (1 mmol) was added. Glacial acetic acid (0.5 mL) as catalyst was added dropwise with stirring. The obtained mixture was then irradiated in microwave oven for 9-13 min, cool to room temperature, the separated precipitate was filted and recrystallized from 96 % ethanol to yield the title compounds **4**.

4-Formyl-7-methylcoumarin 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone (4a): Yellow solid, m.p. 150-152 ºC, yield 65 %; IR (KBr, ν_{max}, cm^{-1}): 3456, 3259, 1747, 1720, 1617, 1528, 1500, 1490, 1211, 1044, 1090; ^{1}H NMR (DMSO-d_6) ⅆ (ppm): 8.47 (s, 1H, CH=N), 12.23 (s, 1H, NH-2), 9.12 (d, 1H, *J* = 9.5 Hz, NH-4), 6., 00 (t, 1H, *J* = 9.25 Hz, H-1'), 5.34 (t, 1H, *J* = 9.25 Hz, H-2'), 5.43 (t, 1H, *J* = 9.5 Hz, H-3'), 4.98 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* =

12.5, 4.75 Hz, H-6'a), 3.99 (dd, 1H, *J* = 12.25, 1.75 Hz, H-6'b), 4.11 (ddd, 1H, *J* = 9.88, 4.63, 2.22 Hz, H-5'), 7.81 (d, 1H, *J* = 9.5 Hz, H-5"), 7.29-7.27 (m, 2H, H-8" & H-6"), 7.20 (s, 1H, H-3"), 2.00-1.94 (s, 12H, CH_3CO), 2.43 (s, 3H, 7"-CH_3), ^{13}C NMR (DMSO-d_6) δ (ppm): 137.1 (CH=N), 179.0 (C=S), 170.0-169.3 (CH_3CO ester), 160.1 (C=O lacton), 81.7 (C-1'), 70.8 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.4 (C-5'), 61.7 (C-6'), 114.5 (C-3"), 143.1 (C-4"), 117.0 (C-4"a), 125.8 (C-5"), 124.4 (C-6"), 144.3 (C-7"), 111.5 (C-8"), 153.6 (C-8"a), 20.5-20.3 (CH_3CO ester), 21.0 (CH_3, 7"-methyl); ESI-MS: $C_{26}H_{29}N_3O_{11}S$, calcd. for $[M-H]^+$ = 590 Da, found: *m/z* 590.

4-Formyl-7-ethoxycoumarin 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone (4b): Yellow solid, m.p. 137-140 ºC, yield 67 %; IR (KBr, ν_{max}, cm^{-1}) : 3563, 3299, 1730, 1614, 1526, 1500, 1490, 1248, 1063, 1100; ^{1}H NMR (DMSO-d_6) δ (ppm): 8.45 (s, 1H, CH=N), 12.22 (s, 1H, NH-2), 9.12 (d, 1H, *J* = 9.5 Hz, NH-4), 5.99 (t, 1H, *J* = 9.25 Hz, H-1'), 5.35 (t, 1H, *J* = 9.25 Hz, H-2'), 5.43 (t, 1H, *J* = 9.5 Hz, H-3'), 4.97 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* = 12.5, 4.5, H-6'a), 3.99 (dd, 1H, *J* = 12.25, 1.75 Hz, H-6'b), 4.11 (ddd, 1H, *J* = 10.0, 4.5, 2.5 Hz, H-5'), 7.83 (d, 1H, *J* = 9.5 Hz, H-5"), 7.02 (d, 1H, *J* = 2.5 Hz, H-8"), 7.03 (dd, 1H, *J* = 9.5, 2.5 Hz, H-6"), 7.07 (s, 1H, H-3"), 2.00-1.94 (s, 12H, CH_3CO ester), 1.36 (t, 3H, *J* = 7.0 Hz, CH_3, 7"-ethoxy), 4.11 (q, 2H, *J* = 7.0 Hz, CH_2O, 7"-ethoxy); ^{13}C NMR (DMSO-d_6) δ (ppm): 137.3 (CH=N), 179.0 (C=S), 169.9-169.3 (CH_3CO ester), 160.2 (C=O lacton), 81.6 (C-1'), 70.8 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.3 (C-5'), 61.7 (C-6'), 109.2 (C-3"), 144.3 (C-4"), 110.2 (C-4"a), 125.8 (C-5"), 112.9 (C-6"), 161.7 (C-7"), 101.6 (C-8"), 155.5 (C-8"a), 20.5-20.3 (CH_3CO ester), 64.0 (OCH_2, 7"-ethoxy), 14.3 (CH_3, 7"-ethoxy); ESI-MS: $C_{27}H_{31}N_3O_{12}S$, calcd. for $[M-H]^+$ = 620 Da, found: *m/z* 620.

4-Formyl-7-propoxycoumarin 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone (4c): Yellow solid, m.p. 173-175 ºC, yield 65 %; IR (KBr, ν_{max}, cm^{-1}): 3559, 3347, 3220, 1743, 1612, 1534, 1233, 1044, 1090; ^{1}H NMR (DMSO-d_6) δ (ppm): 8.44 (s, 1H, CH=N), 12.22 (s, 1H, NH-2), 9.10 (d, 1H, *J* = 9.0 Hz, NH-4), 5.99 (t, 1H, *J* = 9.25 Hz, H-1'), 5.35 (t, 1H, *J* = 9.25 Hz, H-2'), 5.43 (t, 1H, *J* = 9.25 Hz, H-3'), 4.97 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* = 12.5, 4.5 Hz, H-6'a), 3.99 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6'b), 4.11 (ddd, 1H, *J* = 12.0, 4.5, 2.0 Hz, H-5'), 7.84 (d, 1H, *J* = 8.0 Hz, H-5"), 7.04 (d, 1H, *J* = 2.5 Hz, H-8"), 7.03 (dd, 1H, *J* = 8.0, 2.5 Hz, H-6"), 7.06 (s, 1H, H-3"), 2.00-1.94 (s, 12H, CH_3CO ester), 0.99 (t, 3H, *J* = 7.5 Hz, CH_3-, 7"-propoxy), 1.76 (sextet, 2H, *J* = 7.5 Hz, -CH_2-, 7"-propoxy), 4.05 (t, 2H, *J* = 6.5 Hz, -CH_2O-, 7"-propoxy); ^{13}C NMR (DMSO-d_6) δ (ppm): 137.4 (CH=N), 179.0 (C=S), 169.9-169.3 (CH_3CO ester), 160.3 (C=O lacton), 81.6 (C-1'), 70.8 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.3 (C-5'), 61.7 (C-6'), 109.2 (C-3"), 144.4 (C-4"), 110.3 (C-4"a), 125.8 (C-5"), 112.9 (C-6"), 161.9 (C-7"), 101.6 (C-8"), 155.5 (C-8"a), 20.5-20.3 (CH_3CO ester), 69.8 (OCH_2, 7"-propoxy), 21.8 (CH_2, 7"- propoxy), 10.2 (CH_3, 7"-propoxy); ESI-MS: $C_{28}H_{33}N_3O_{12}S$, calcd. for $[M-H]^+$ = 634 Da, found: *m/z* 634.

4-Formyl-7-butoxycoumarin 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone (4d): Yellow solid, m.p. 177-179 ºC, yield 70 %; IR (KBr, ν_{max}, cm^{-1}): 3502, 3267, 1748, 1721, 1614, 1524, 1500, 1233, 1039, 1090; 1H NMR (DMSO-d_6) δ (ppm): 8.53 (s, 1H, CH=N), 12.29 (s, 1H, NH-2), 9.10 (d, 1H, *J* = 9.5 Hz, NH-4), 5.99 (t, 1H, *J* = 9.25 Hz, H-1'), 5.35 (t, 1H, *J* = 9.25 Hz, H-2'), 5.42 (t, 1H, *J* = 9.25 Hz, H-3'), 4.97 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* = 12.5, 5.0 Hz, H-6'a), 3.99 (dd, 1H, *J* = 10.5 Hz, H-6'b), 4.12-4.08 (m, 1H, H-5'), 7.84 (d, 1H, *J* = 8.5 Hz, H-5"), 7.05-7.02 (m, 2H, H-8"), 7.05-7.02 (m, 2H, H-6"), 7.06 (s, 1H, H-3"), 2.00-1.91 (s, 12H, CH_3CO ester), 0.93 (t, 3H, *J* = 7.5 Hz, CH_3, 7"-butoxy), 1.44 (sextet, H, *J* = 7.5 Hz, CH_2, 7"- butoxy), 4.09 (q, 2H, *J* = 6.5 Hz, CH_2O, 7"-butoxy); ^{13}C NMR (DMSO-d_6) δ (ppm): 137.4 (CH=N), 179.0 (C=S), 170.0-169.3 (CH_3CO ester), 160.3 (C=O lacton), 81.6 (C-1'), 70.8 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.4 (C-5'), 61.7 (C-6'), 109.0 (C-3"), 147.4 (C-4"), 110,3 (C-4"a), 101.5 (C-5"), 161.9 (C-6"), 112.9 (C-7"), 125.8 (C-8"), 155.5 (C-8"a), 20.5-20.3 (CH_3CO ester), 68.0 (OCH_2, 7"-butoxy), 30.5 (CH_2, 7"-butoxy), 18.6 (CH_2, 7"-butoxy), 13.6 (CH_3, 7"-butoxy); ESI-MS: $C_{29}H_{35}N_3O_{12}S$, calcd. for $[M-H]^+$ = 648 Da, found: *m/z* 648.

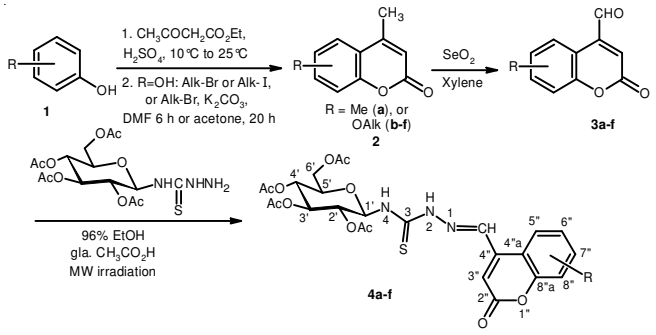
4-Formyl-6-ethoxycoumarin 4-(2,3,4,6-tetra-O-acetyl-ß-D-glucopyranosyl)thiosemicarbazone (4e): Yellow solid, m.p. 189-193 ºC, yield 79 %; IR (KBr, ν_{max}, cm^{-1}): 3593, 3249, 1760, 1716, 1600, 1523, 1500, 1242, 1034, 1090; ^{1}H NMR (DMSO-d_6) δ (ppm): 8.57(s, 1H, CH=N), 9.19 (d, 1H, *J* = 9.5 Hz, NH-2), 12.12 (s, 1H, NH-4), 6.03 (t, 1H, *J* = 9.25 Hz, H-1'), 5.30 (t, 1H, *J* = 9.25 Hz, H-2'), 5.43 (t, 1H, *J* = 9.5 Hz, H-3'), 4.97 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* = 12.5, 4.5 Hz, H-6'a), 3.99 (dd, 1H, *J* = 12.25, 1.5 Hz, H-6'b), 4.14-4.08 (m, 1H, H-5'), 7.28-7.25 (m, 1H, H-5"), 7.40 (d, 1H, *J* = 9.0 Hz, H-8"), 7.32(s, 1H, H-3"), 2.00-1.93 (s, 12H, CH_3CO ester), 1.37 (t, 3H, *J* = 7.0 Hz, CH_3, 6"-ethoxy), 4.10 (q, 2H, *J* = 7.0 Hz, CH_2O, 6"-ethoxy); ^{13}C NMR (DMSO-d_6) δ (ppm): 136.7 (CH=N), 178.9 (C=S), 170.0-169.3 (CH_3CO ester), 160.1 (C=O lacton), 81.7 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.4 (C-5'), 61.8 (C-6'), 107.5 (C-3"), 147.7 (C-4"), 136.7 (C-4"a), 111.8 (C-5"), 154.8 (C-6"), 117.5 (C-7"), 118.0 (C-8"), 154.8 (C-8"a), 20.5-20.3 (CH_3CO ester), 63.7 (OCH_2, 6"-ethoxy), 14.5 (CH_3, 6"-ethoxy); ESI-MS: $C_{27}H_{31}N_3O_{12}S$, calcd. for $[M-H]^+$ = 620 Da, found: *m/z* 620.

4-Formyl-6-propoxycoumarin 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone (4f): Yellow solid, m.p. 121-135 ºC, yield 69 %; IR (KBr, ν_{max}, cm^{-1}): 3532, 3312, 1750, 1729, 1600, 1562, 1522, 1500, 1243, 1036, 1090; ^{1}H NMR (DMSO-d_6) δ (ppm): 8.55 (s, 1H, CH=N), 9.19 (d, 1H, *J* = 9.0 Hz, NH-2), 12.09 (s, 1H, NH-4), 6.03 (t, 1H, *J* = 9.0 Hz, H-1'), 5.30 (t, 1H, *J* = 9.25 Hz, H-2'), 5.43 (t, 1H, *J* = 9.5 Hz, H-3'), 4.97 (t, 1H, *J* = 9.75 Hz, H-4'), 4.23 (dd, 1H, *J* = 12.5, 4.5 Hz, H-6'a), 4.02-3.98 (m, 1H, H-6'b), 4.13 (ddd, 1H, *J* = 10.0, 4.5, 2.0 Hz, H-5'), 7.28-7.26 (m, 1H, H-5"), 7.40 (d, 1H, *J* = 9.0 Hz, H-8"), 7.33 (s, 1H, H-3"), 2.00-1.93 (s, 12H, CH_3CO ester), 1.01 (t, 3H, *J* = 7.0 Hz, CH_3, 6"-propoxy), 1.77 (sextet, 2H, *J* = 7.0 Hz, CH_2, 6"-propoxy), 4.00 (q, 2H, *J* = 7.0 Hz, CH_2O, 6"-propoxy); ^{13}C NMR (DMSO-d_6) δ (ppm): 136.7 (CH=N), 178.9 (C=S), 170.0-169.3 (CH_3CO ester), 160.1 (C=O lacton), 81.7 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 67.8 (C-4'), 72.4 (C-5'), 61.8 (C-6'), 107.5 (C-3"), 147.8 (C-4"), 136.7 (C-4"a), 111.9 (C-5"), 155.0 (C-6"), 117.5 (C-7"), 119.9 (C-8"), 154.8 (C-8"a), 20.5-20.3 (CH_3CO ester), 69.6 (OCH_2,

6"-propoxy), 22.0 (CH_2, 6"-propoxy), 10.3 (CH_3, 6"-propoxy); ESI-MS: $C_{28}H_{33}N_3O_{12}S$, calcd. for $[M-H]^+$ = 634 Da, found: *m/z* 634.

RESULTS AND DISCUSSION

The compounds of 6- or 7-substituted 4-formylcoumarins **3a-f** that need for study have been synthesized from corresponding substituted 4-methylcoumarins **2a-f** by oxidation it using selenic oxide in boiling xylene[21]. Structures of these 4-formylcoumarins were confirmed using IR spectra by the presence of absorption band at 1708-1694 cm^{-1} due to stretching vibration of aldehyde carbonyl group. All alkoxy-4-methylcoumarins were synthesized by nucleophilic substitution reaction of corresponding hydroxy-4-methylcoumarins with alkyl iodides or bromides. Reaction was carried out in the presence of anhydrous potassium carbonate in acetone (20 h in refluxing) or DMF (6 h in refluxing) (**Scheme-I**).



Scheme-I: Synthetic path for substituted 4-formylcoumarin 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones

Condensation reaction of 6- or 7-substituted 4-formylcou-marins **3a-f** with 4-(tetra-*O*-acetyl-β-D-glucopyranosyl) thiosemicarbazide was carried out on refluxing in the presence of glacial acetic acid as catalyst. Solvent for these reactions are 96 % ethanol. We realized that 96 % ethanol is better solvent than absolute one for these reactions to obtain higher yields. These reactions were executed under microwave-assisted heating method. Reaction product usually seperated as coloured solid after cooling to room temperature. It could be soluble in common organic solvents, such as toluene, ethanol, methanol, DMF, acetone, ethyl acetate.

IR spectra show the characteristic absorption bands at ν = 1750-1730 cm^{-1} ($\nu_{C=O}$ ester), 1259-1211 and 1049-1036 cm^{-1} (ν_{COC} ester), 1743-1720 cm^{-1} ($\nu_{C=O}$ lactone), 1617-1600 cm^{-1} ($\nu_{CH=N}$), 1100-1090 cm^{-1} ($\nu_{C=S}$) and some bands at 1597-1490 cm^{-1} ($\nu_{C=C}$ aromatic). The evidences that confirm the success of reactions are the absence of formyl group -CH=O band in IR spectra at 1708-1694 cm^{-1} and chemical shifts of NH and NH_2 (in thiosemicarbazide) at δ = 9.23, 8.17 and 4.58 ppm (in ^1H NMR spectra).

The assignments of ^1H and ^{13}C were confirmed using COSY, HMBC and HSQC methods in case of compound **4b** (R = 7"-OEt). The ^1H NMR spectra of the 6- or 7-substituted-4-formylcoumarin 4-(tetra-*O*-acetyl-β-D-glucopyranosyl) thiosemicarbazones (**4a-f**) showed resonance signals for proton NH-2 at δ = 12.23-12.22 ppm (in singlet), for proton NH-4 at δ = 9.12-9.10 ppm (in doublet) with coupling constants ^3J = 9.0-9.5 Hz. Protons in glucopyranose ring have resonance signals in range at δ = 6.00-3.99 ppm. protons H-1' and H-2' of pyranose ring had chemical shifts at 6.00-5.99 and 5.35-5.34 ppm, respectively. The β anomeric configuration of **4a-f** was demonstrated on the basis of the coupling constant $J_{1,2}$ = ~9.25 Hz in agreement with the 1,2-*trans*-diaxial relationships between protons H-1' and H-2'. Methyl groups in acetate ester have chemical shifts in range at δ = 2.00-1.94 ppm in singlet, usually as a set of four signals.

Conclusion

In conclusion, an efficient method for synthesis of 6- or 7-substituted 4-formylcoumarin 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones under microwave-assisted refluxing conditions have been performed. Product yields attained 60-79 %.

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