

Synthesis of Some Peracetylated Glucopyranosyl Thiosemicarbazones of Substituted 4-Formylcoumarins

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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 using microwave-assisted heating method. The synthesized compounds were characterized by FT-IR and ^1H 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 number of diseases such as heart disease¹⁻³, lymphoedema and other high-protein edemas⁴. They have also found pharmaceutical applications in the treatment of patients with chronic venous insufficiency⁵, skin cancer⁶, renal cell carcinoma⁷, prostate cancer⁸ as well as in the treatment of thermal injuries⁹. They may also be useful in preventing oxidative stress and apoptosis in HIV infection¹⁰.

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 glucopyranosyl thiosemicarbazones were synthesized^{15,16}. Some peracetylated glucopyranosyl 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 lab¹⁷. Continuing our works on glucopyranosyl thiosemicarbazones¹⁸⁻²⁰, 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). ^1H and

^{13}C NMR spectra were recorded on Bruker Avance spectrometer AV500 (Bruker, Germany) at 500.13 MHz and 125.77 MHz, respectively, using $\text{DMSO}-d_6$ as solvent and TMS as an internal standard. MS spectra were recorded on mass spectrometer LTQ Orbitrap XLTM (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 isothiocyanate¹⁶. 4-Formyl-6-(or 7-)-methyl/alkoxy-4-formylcoumarins were synthesized based on the synthetic method for 4-formyl-7-methoxycoumarin²¹.

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 filtered 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 °C, yield 65 %; IR (KBr, ν_{max} , cm^{-1}): 3456, 3259, 1747, 1720, 1617, 1528, 1500, 1490, 1211, 1044, 1090; ^1H NMR ($\text{DMSO}-d_6$) δ (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, CH₃CO), 2.43 (s, 3H, 7''-CH₃), ¹³C NMR (DMSO-*d*₆) δ (ppm): 137.1 (CH=N), 179.0 (C=S), 170.0-169.3 (CH₃CO 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 (CH₃CO ester), 21.0 (CH₃, 7''-methyl); ESI-MS: C₂₆H₂₉N₃O₁₁S, 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 °C, yield 67 %; IR (KBr, $\nu_{\max}$, cm⁻¹): 3563, 3299, 1730, 1614, 1526, 1500, 1490, 1248, 1063, 1100; ¹H 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, $J = 12.5, 4.5$ Hz, 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, CH₃CO ester), 1.36 (t, 3H, $J = 7.0$ Hz, CH₃, 7''-ethoxy), 4.11 (q, 2H, $J = 7.0$ Hz, CH₂O, 7''-ethoxy); ¹³C NMR (DMSO-*d*₆) δ (ppm): 137.3 (CH=N), 179.0 (C=S), 169.9-169.3 (CH₃CO 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 (CH₃CO ester), 64.0 (OCH₂, 7''-ethoxy), 14.3 (CH₃, 7''-ethoxy); ESI-MS: C₂₇H₃₁N₃O₁₂S, 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 °C, yield 65 %; IR (KBr, $\nu_{\max}$, cm⁻¹): 3559, 3347, 3220, 1743, 1612, 1534, 1233, 1044, 1090; ¹H 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, CH₃CO ester), 0.99 (t, 3H, $J = 7.5$ Hz, CH₃, 7''-propoxy), 1.76 (sextet, 2H, $J = 7.5$ Hz, -CH₂-, 7''-propoxy), 4.05 (t, 2H, $J = 6.5$ Hz, -CH₂O-, 7''-propoxy); ¹³C NMR (DMSO-*d*₆) δ (ppm): 137.4 (CH=N), 179.0 (C=S), 169.9-169.3 (CH₃CO 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 (CH₃CO ester), 69.8 (OCH₂, 7''-propoxy), 21.8 (CH₂, 7''-propoxy), 10.2 (CH₃, 7''-propoxy); ESI-MS: C₂₈H₃₃N₃O₁₂S, 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 °C, yield 70 %; IR (KBr, $\nu_{\max}$, 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, CH₃CO ester), 0.93 (t, 3H, $J = 7.5$ Hz, CH₃, 7''-butoxy), 1.44 (sextet, H, $J = 7.5$ Hz, CH₂, 7''-butoxy), 4.09 (q, 2H, $J = 6.5$ Hz, CH₂O, 7''-butoxy); ¹³C NMR (DMSO-*d*₆) δ (ppm): 137.4 (CH=N), 179.0 (C=S), 170.0-169.3 (CH₃CO 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 (CH₃CO ester), 68.0 (OCH₂, 7''-butoxy), 30.5 (CH₂, 7''-butoxy), 18.6 (CH₂, 7''-butoxy), 13.6 (CH₃, 7''-butoxy); ESI-MS: C₂₉H₃₅N₃O₁₂S, calcd. for [M-H]⁺ = 648 Da, found: m/z 648.

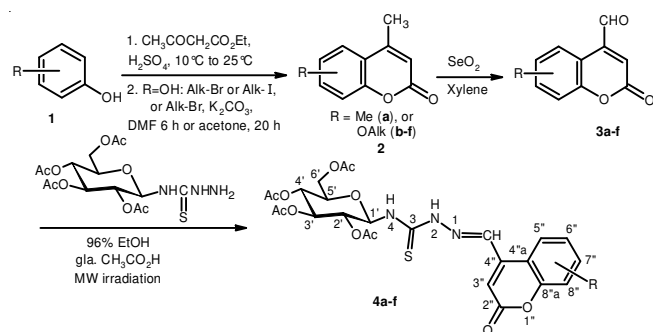
4-Formyl-6-ethoxycoumarin 4-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)thiosemicarbazone (4e): Yellow solid, m.p. 189-193 °C, yield 79 %; IR (KBr, $\nu_{\max}$, cm⁻¹): 3593, 3249, 1760, 1716, 1600, 1523, 1500, 1242, 1034, 1090; ¹H NMR (DMSO-*d*₆) δ (ppm): 8.57 (s, 1H, CH=N), 9.19 (d, 1H, $J = 9.5$ 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, CH₃CO ester), 1.37 (t, 3H, $J = 7.0$ Hz, CH₃, 6''-ethoxy), 4.10 (q, 2H, $J = 7.0$ Hz, CH₂O, 6''-ethoxy); ¹³C NMR (DMSO-*d*₆) δ (ppm): 136.7 (CH=N), 178.9 (C=S), 170.0-169.3 (CH₃CO 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 (CH₃CO ester), 63.7 (OCH₂, 6''-ethoxy), 14.5 (CH₃, 6''-ethoxy); ESI-MS: C₂₇H₃₁N₃O₁₂S, 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 °C, yield 69 %; IR (KBr, $\nu_{\max}$, cm⁻¹): 3532, 3312, 1750, 1729, 1600, 1562, 1522, 1500, 1243, 1036, 1090; ¹H 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, CH₃CO ester), 1.01 (t, 3H, $J = 7.0$ Hz, CH₃, 6''-propoxy), 1.77 (sextet, 2H, $J = 7.0$ Hz, CH₂, 6''-propoxy), 4.00 (q, 2H, $J = 7.0$ Hz, CH₂O, 6''-propoxy); ¹³C NMR (DMSO-*d*₆) δ (ppm): 136.7 (CH=N), 178.9 (C=S), 170.0-169.3 (CH₃CO 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 (CH₃CO ester), 69.6 (OCH₂,

6"-propoxy), 22.0 (CH₂, 6"-propoxy), 10.3 (CH₃, 6"-propoxy); ESI-MS: C₂₈H₃₃N₃O₁₂S, 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 xylene²¹. 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-formylcoumarins **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 separated 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 $\nu = 1750\text{--}1730\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$ ester), $1259\text{--}1211$ and $1049\text{--}1036\text{ cm}^{-1}$ (ν_{COC} ester), $1743\text{--}1720\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$ lactone), $1617\text{--}1600\text{ cm}^{-1}$ ($\nu_{\text{CH=N}}$), $1100\text{--}1090\text{ cm}^{-1}$ ($\nu_{\text{C=S}}$) and some bands at $1597\text{--}1490\text{ cm}^{-1}$ ($\nu_{\text{C=C}}$ aromatic). The evidences that confirm the success of reactions are the absence of formyl group -CH=O band in IR spectra at $1708\text{--}1694\text{ cm}^{-1}$ and chemical shifts of NH and NH₂ (in thiosemicarbazide) at $\delta = 9.23$, 8.17 and 4.58 ppm (in ¹H NMR spectra).

The assignments of ¹H and ¹³C 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 $\delta = 12.23\text{--}12.22$ ppm (in singlet), for proton NH-4 at $\delta = 9.12\text{--}9.10$ ppm (in doublet) with coupling constants ³*J* = $9.0\text{--}9.5$ Hz. Protons in glucopyranose ring have resonance signals in range at $\delta = 6.00\text{--}3.99$ ppm. protons H-1' and H-2' of pyranose ring had chemical shifts at $6.00\text{--}5.99$ and $5.35\text{--}5.34$ 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 $\delta = 2.00\text{--}1.94$ 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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