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SYNTHESIS OF SOME ACETOPHENONE (PER-*O*-ACETYL-*β*-MALTOSYL)-THIOSEMICARBAZONES

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ABSTRACT

A series of per-O-acetyl-β-D-glycosyl thiosemicarbazones of acetophenones were obtained from reaction of per-O-acetyl-β-D-glycosyl isothiocyanates with corresponding acetophenones in ethanol or acetic acid as solvent using microwave-assisted. Structures of thiosemicarbazones were confirmed by spectroscopic methods.

I - INTRODUCTION

Chemistry of per-*O*-acetyl-β-D-glycosyl isothiocyanates have been studied in our lab in several years [1]. The chemistry of thiosemicarbazide derivatives of saccharides is interested [2]. These compounds arouse interest as versatile intermediates for preparing various (e.g., heterocyclic) derivatives as well. Thiosemicarbazones can be used for making electrodes, or complexes formation of metallic ions [3]. Thiosemicarbazones exhibit various biological activities such as antituberculosis, antimicrobial, anti-inflammatory, antiviral, anticonvulsant, and antihypertensive, and local anesthetic, anticancer, hypoglycemic and cytotoxic activities, among others [4].

In previous papers, we have studied the synthesis and reactivity of some peracetated glycopyranosyl thiosemicarbazones with several different aromatic or heterocyclic carbonyl compounds [1a,b,g,n]. We reported herein the synthesis of some new substituted acetophenone per-hepta-*O*-acetyl-β-maltosyl thiosemicarbazones using microwave-assisted method [5].

II - EXPERIMENTAL

Melting points were determined on a STUART SMP3 apparatus (BIBBY STERILIN-UK). The IR spectra were recorded on a Magna 760 FT-IR Spectrometer (NICOLET, USA) in KBr disc. The ^{1}H NMR (at 500.13 MHz) and ^{13}C NMR (at 125.77 MHz) spectra were recorded on an AVANCE Spectrometer AV500 (BRUKER, Germany) in DMSO-d_6 solution in ppm compared to TMS as internal reference.

General synthetic method of substituted acetophenone (hepta-O-acetyl-β-maltosyl)-thiosemicarbazones (**4a-l**). A mixture of hepta-*O*-acetyl-β-maltosyl thiosemicarbazide **1** (1 mmol), acetophenones **2** (1 mmol) and glacial acetic acid (0.5 mL) in absolute ethanol (in the presence of glacial acetic acid as catalyst) or glacial acetic acid (20 mL) was heated at reflux using domestic microwave oven TIFANY 750W in 5-7 min. In case of ethanol as solvent, the solvent was evaporated to one half the original volumes. The resulting colorless crystals were filtered by suction. In case of acetic acid as solvent, the water was added, and then the precipitate was filtered by suction. The crude product when recrystallized from 95%

ethanol to afford the title compounds **3**. Some selected ^{1}H NMR and ^{13}C NMR spectra of compounds **3** are as follows:

Compound 3b (R=4-NO_2): ^{1}H NMR (DMSO-d_6): δ 11.01 (s, 1H, NH), 8.71 (d, 1H, *J* 9.0 Hz, NH), 8.30 (d, 2H, *J* 8.5 Hz, H-3 & H-5 aromatic), 8.16 (d, 2H, *J* 8.9 Hz, H-2 & H-6 aromatic), 5.89 (t, 1H, *J* 9.0 Hz, H-1), 5.48 (t, 1H, *J* 9.0 Hz, H-3), 5.33 (d, 1H, *J* 2.5 Hz, H-1'), 5 .25 (t, 1H, *J* 9.75 Hz, H-3'), 5.21 (t, 1H, *J* 9.25 Hz, H-2), 5.00 (t, 1H, *J* 9.75 Hz, H-4'), 4.88 (dd, 1H, *J* 10.0 Hz, *J* 3.0 Hz, H-5'), 4.34 (d, 1H, *J* 11.5 Hz, H-6'a), 4.21–4.16 (m, 2H, H-6'b, H-6a), 4.03–3.92 (m, 3H, H-5, H-6b, H-2'), 3.93 (t, *J* 9.0 Hz, 1H, H-4), 2.38 (s, 3H, C=N–CH_3), 2.05–1.93 (7s, 21H, 7×*CH_3*CO); ^{13}C NMR (DMSO-d_6): δ 179.75 (C=S), 170.40–169.14 (7×C=O), 156.07 (C-4 aromatic), 147.65 (C=N), 143.54 (C-1 aromatic), 127.89 (C-2 & C-6 aromatic), 123.60 (C-3 & C-5 aromatic), 95.38 (C-1'), 81.09 (C-1), 74.41 (C-3), 73.88 (C-4), 72.91 (C-5), 71.32 (C-2), 69.53 (C-5'), 68.91 (C-3'), 68.01 (C-2'), 67.82 (C-4'), 62.86 (C-6'), 61.45 (C-6), 20.59-20.24 (7s, 21H, 7×*CH_3*CO), 15.03 (C=N–CH_3).

Compound 3b' (R=4-NO_2): ^{1}H NMR (DMSO-d_6): δ 11.01 (s, 1H, NH), 8.71 (d, 1H, *J* 9.0 Hz, NH), 8.21 (d, 2H, *J* 8.0 Hz, H-3 & H-5 aromatic), 8.17 (d, 2H, *J* 8.0 Hz, H-2 & H-6 aromatic), 5.89 (t, 1H, *J* 9.0 Hz, H-1), 5.48 (t, 1H, *J* 9.0 Hz, H-3), 5.33 (d, 1H, *J* 2.5 Hz, H-1'), 5.25 (t, 1H, *J* 9.75 Hz, H-3'), 5.21 (t, 1H, *J* 9.25 Hz, H-2), 5.00 (t, 1H, *J* 9.75 Hz, H-4'), 4.88 (dd, 1H, *J* 10.0 Hz, *J* 3.0 Hz, H-5'), 4.34 (d, 1H, *J* 11.5 Hz, H-6'a), 4.21–4.16 (m, 2H, H-6'b, H-6a), 4.03–3.92 (m, 3H, H-5, H-6b, H-2'), 3.93 (t, *J* 9.0 Hz, 1H, H-4), 2.32 (s, 3H, C=N–CH_3), 2.05–1.93 (7s, 21H, 7×*CH_3*CO); ^{13}C NMR (DMSO-d_6): δ 179.75 (C=S), 170.40–169.14 (7×C=O), 148.10 (C-4 aromatic), 147.18 (C=N), 143.31 (C-1 aromatic), 127.85 (C-2 & C-6 aromatic), 123.24 (C-3 & C-5 aromatic), 95.38 (C-1'), 81.09 (C-1), 74.41 (C-3), 73.88 (C-4), 72.91 (C-5), 71.32 (C-2), 69.53 (C-5'), 68.91 (C-3'), 68.01 (C-2'), 67.82 (C-4'), 62.86 (C-6'), 61.45 (C-6), 20.59-20.24 (7s, 21H, 7×*CH_3*CO), 14.40 (C=N–CH_3). Ratio of **3b** and **3b'**: 62.77% and 37.23%.

Compound 3c (R=3-NO_2): δ 10.97 (s, 1H, NH), 8.67 (d, 1H, *J* 9.5 Hz, NH), 8.55 (s, 1H, H-2 aromatic), 8.39 (d, 1H, *J* 8.0 Hz, H-6 aromatic), 8.25 (dd, 2H, *J* 8.25 Hz, *J* 2.25 Hz, H-4 aromatic), 7.03 (t, 1H, *J* 8.0 Hz, H-5 aromatic), 5.88 (t, 1H, *J* 9.25 Hz, H-1), 5.47 (t, 1H, *J* 9.25 Hz, H-3), 5.32 (d, 1H, *J* 4.0 Hz, H-1'), 5.24 (t, 1H, *J* 10.0 Hz, H-3'), 5.15 (t, 1H, *J* 9.25 Hz, H-2), 4.99 (t, 1H, *J* 9.75 Hz, H-4'), 4.88 (dd, 1H, *J* 10.5 Hz, *J* 4.0 Hz, H-5'), 4.35 (d, 1H, *J* 10.5 Hz, H-6'a), 4.22 - 4.14 (m, 2H, H-6'b, H-6a), 4.03 - 3.92 (m, 3H, H-5, H-2', H-6'b), 3.96 (t, 1H, *J* 9.75 Hz, H-4), 2.40 (s, 3H, C=N–CH_3), 2.05 - 1.93 (7s, 21H, 7×*CH_3*CO); ^{13}C NMR (DMSO-d_6): δ 179.6 (C=S), 170.0 - 169.1 (7C, 7×*CO*CH_3), 148.1 (C-1‴), 147.6 (*C*=N), 139.2 (C-6‴), 132.9 (C-2‴), 129.7 (C-3‴), 123.9 (C-4‴), 121.2 (C-5‴), 93.4 (C-1″), 81.1 (C-1′), 74.3 (C-3′), 73.8 (C-4′), 72.9 (C-5′), 71.2 (C-3″), 69.5 (C-5″), 68.9 (C-2′), 67.9 (C-2″), 67.7 (C-4″), 62.8 (C-6″), 61.4 (C-6′), 21.6 - 20.2 (7C, 7×CO*CH_3*), 14.5 (C=N–*CH_3*).

Compound 3e (R=3-NO_2-4-OMe): ^{1}H NMR (DMSO-d_6): δ 10.84 (s, 1H, NH), 8.61 (d, 1H, *J* 9.0 Hz, NH), 8.31 (d, 1H, *J* 2.5 Hz, H-2 aromatic), 8.19 (dd, 1H, *J* 9.0 Hz, *J* 2.5 Hz, H-6 aromatic), 7.38 (d, 1H, *J* 9.0 Hz, H-5 aromatic), 5.87 (t, 1H, *J* 9.25 Hz, H-1), 5.47 (t, 1H, *J* 9.25 Hz, H-3), 5.32 (d, 1H, *J* 3.75 Hz, H-1'), 5.25 (t, 1H, *J* 9.95 Hz, H-3'), 5.14 (t, 1H, *J* 9.25 Hz, H-2), 5.00 (t, 1H, *J* 9.95 Hz, H-4'), 4.88 (dd, 1H, *J* 10.2 Hz, *J* 3.75 Hz, H-5'), 4.35 (dd, 1H, *J* 12.2 Hz, *J* 2.3 Hz, H-6'a), 4.21 (dd, 1H, *J* 12.2 Hz, *J* 5.0 Hz, H-6'b), 4.17 (dd, 1H, *J* 12.7 Hz, *J* 4.85 Hz, H-6a), 4.04 - 3.96 (m, 4H, H-5, H-6b, H-2', H-4), 3.98 (s, 3H, O-CH_3), 2.34 (s, 3H, C=N–CH_3), 1.94 - 2.06 (7s, 21H, 7×*CH_3*CO); ^{13}C NMR (DMSO-d_6): δ 179.35 (C=S), 169.89 - 169.01 (7×C=O), 152.22 (C-4 aromatic), 147.58 (C=N), 139.61 (C-3 aromatic), 131.98 (C-6 aromatic), 129.81 (C-1 aromatic), 122.49 (C-2 aromatic), 113.84 (C-5 aromatic), 95.27 (C-1'), 81.02 (C-1), 74.22 (C-3), 73.90 (C-4), 72.91 (C-5), 71.14 (C-2), 69.47 (C-5'), 68.86 (C-3'), 67.91 (C-2'), 67.81 (C-4'), 62.76 (C-6'), 61.40

(C-6), 56.84 (4-OCH_3), 20.46 - 20.12 (7×CH_3CO), 14.13 (C=N–CH_3).

Compound 3f (R=3-NO_2-4-OEt): ^{1}H NMR (DMSO-d_6): δ 10.83 (s, 1H, NH), 8.59 (d, 1H, *J* 9.0 Hz, NH), 8.28 (d, 1H, *J* 2.5 Hz, H-2 aromatic), 8.14 (dd, 1H, *J* 9.0 Hz, *J* 2.25 Hz, H-6 aromatic), 7.34 (d, 1H, *J* 9.0 Hz, H-5 aromatic), 5.85 (t, 1H, *J* 9.0 Hz, H-1), 5.45 (t, 1H, *J* 9.25 Hz, H-3), 5.30 (d, 1H, *J* 4.0 Hz, H-1'), 5.23 (t, 1H, *J* 10.0 Hz, H-3'), 5.12 (t, 1H, *J* 9.25 Hz, H-2), 4.98 (t, 1H, *J* 9.75 Hz, H-4'), 4.86 (dd, 1H, *J* 10.5, *J* 4.0 Hz, H-5'), 4.34 (dd, 1H, *J* 12.25 Hz, *J* 2.25 Hz, H-6'a), 4.26 (q, 2H, *J* 6.75 Hz, O*CH*$_2$CH$_3$), 4.18 (dd, 1H, *J* 12.25 Hz, *J* 5.0 Hz, H-6'b), 4.15 (dd, 1H, *J* 12.75 Hz, *J* 4.75 Hz, H-6a), 4.02–3.98 (m, 3H, H-5, H-6b, H-2'), 3.92 (t, 1H, *J* 9.5 Hz, H-4), 2.31 (s, 3H, C=N–CH_3), 2.04 - 1.91 (7s, 21H, 7×*CH*$_3$CO), 1.33 (t, 3H, *J* 6.75 Hz, OCH$_2$*CH*$_3$); ^{13}C NMR (DMSO-d_6): δ 179.35 (C=S), 168.99 - 169.88 (7C, 7×C=O), 151.39 (C-4 aromatic), 147.61 (C=N), 129.66 (C-1 aromatic), 139.93 (C-3 aromatic), 131.83 (C-6 aromatic), 122.41 (C-2 aromatic), 114.58 (C-5 aromatic), 95.27 (C-1'), 81.02 (C-1), 74.21 (C-3), 73.90 (C-4), 72.91 (C-5), 71.13 (C-2), 69.46 (C-5'), 68.85 (C-3'), 67.91 (C-2'), 67.81 (C-4'), 65.27 (O–CH_2–), 62.76 (C-6'), 61.40 (C-6), 20.107 - 20.457 (7×CH_3CO), 14.13 (C=N–CH_3), 14.12 (OCH$_2$–CH_3).

Compound 3g (R=4-Cl): ^{1}H NMR (DMSO-d_6): δ 10.84 (s, 1H, NH), 8.59 (d, 1H, *J* 9.05 Hz, NH), 7.93 (d, 2H, *J* 8.5 Hz, H-2 & H-6 aromatic), 7.46 (d, 2H, *J* 8.5 Hz, H-3 & H-5 aromatic), 5.88 (t, 1H, *J* 9.25 Hz, H-1), 5.46 (t, 1H, *J* 9.25 Hz, H-3), 5.32 (d, 1H, *J* 3.5 Hz, H-1'), 5.24 (t, 1H, *J* 10.0 Hz, H-3'), 5.19 (t, 1H, *J* 9.0 Hz, H-2), 4.99 (t, 1H, *J* 9.75 Hz, H-4'), 4.87 (dd, 1H, *J* 10.5 Hz, *J* 3.5 Hz, H-5'), 4.36 - 4.34 (m, 1H, H-6'a), 4.20–4.14 (m, 2H, H-6a, H-6'b), 4.02–3.97 (m, 3H, H-5, H-6b, H-2'), 3.93 (t, 1H, *J* 9.25 Hz, H-4), 2.32 (s, 3H, C=N–CH_3), 2.05–1.92 (7s, 21H, 7×*CH*$_3$CO).

Compound 3h (R=4-Br): ^{1}H NMR (DMSO-d_6): δ 10.85 (s, 1H, NH), 8.58 (d, 1H, *J* 9.0 Hz, NH), 7.85 (d, 2H, *J* 8.5 Hz, H-2 & H-6 aromatic), 7.86 (d, 2H, *J* 8.0 Hz, H-3 & H-5 aromatic), 5.88 (t, 1H, *J* 9.0 Hz, H-1), 5.46 (t, 1H, *J* 9.0 Hz, H-3), 5.32 (d, 1H, *J* 3.5 Hz, H-1'), 5.24 (t, 1H, *J* 10.0 Hz, H-3'), 5.17 (t, 1H, *J* 9.25 Hz, H-2), 4.99 (t, 1H, *J* 9.75 Hz, H-4'), 4.87 (dd, 1H, *J* 10.5 Hz, *J* 3.5 Hz, H-2'), 4.35 (dd, 1H, *J* 11.5 Hz, H-6'a), 4.21–4.14 (m, 2H, H-6'b, H-6a), 4.02 (ddd, 1H, *J* 9.3 Hz, *J* 5.0 Hz, *J* 2.3 Hz, H-5), 4.00 (m, 1H, H-6'b), 3.98 (m, 1H, H-5'), 3.93 (t, 1H, *J* 9.3 Hz, H-4), 2.31 (s, 3H, C=N–CH_3), 2.05–1.92 (7s, 21H, 7×*CH*$_3$CO); ^{13}C NMR (DMSO-d_6): δ 179.38 (C=S), 170.05–169.14 (7×C=O), 148.58 (C=N), 136.56 (C-4 aromatic), 131.18 (C-3 & C-5 aromatic), 128.78 (C-2 & C-6 aromatic), 123.09 (C-1 aromatic), 95.36 (C-1'), 81.02 (C-1), 74.37 (C-3), 73.86 (C-4), 72.87 (C-5), 71.28 (C-2), 69.52 (C-5'), 68.90 (C-3'), 67.99 (C-2'), 67.80 (C-4'), 62.88 (C-6'), 61.44 (C-6), 20.60 - 20.25 (7×CH_3CO), 14.29 (C=N–CH_3).

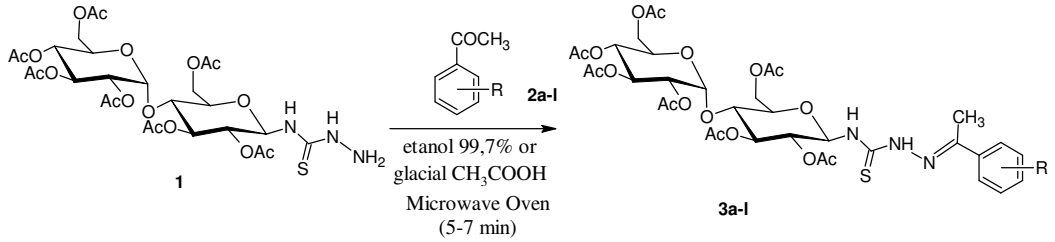
Compound 3k (R=4-OH): ^{1}H NMR (DMSO-d_6): δ 10.66 (s, 1H, NH), 9.81 (s, 1H, OH), 8.43 (d, 1H, *J* 9.5 Hz, NH), 7.74 (d, 2H, *J* 8.5 Hz, H-2 & H-6 aromatic), 6.78 (d, 2H, *J* 8.5 Hz, H-3 & H-5 aromatic), 5.87 (t, 1H, *J* 9.25 Hz, H-1), 5.46 (t, 1H, *J* 9.5 Hz, H-3), 5.30 (d, 1H, *J* 3.5 Hz, H-1'), 5.24 (t, 1H, *J* 10.0 Hz, H-3'), 5.15 (t, 1H, *J* 9.25 Hz, H-2), 4.99 (t, 1H, *J* 9.75 Hz, H-4'), 4.87 (dd, 1H, *J* 10.25 Hz, *J* 3.75 Hz, H-5'), 4.35 (d, 1H, *J* 11.0 Hz, H-6'a), 4.18 (t, 1H, *J* 12.75 Hz, H-6'b), 4.17 (t, 1H, *J* 12.25 Hz, H-6a), 4.03–3.99 (m, 3H, H-5, H-6b, H-2'), 3.96 (t, 1H, *J* 8.5 Hz, H-4), 2.26 (s, 3H, C=N–CH_3), 2.05–1.93 (7s, 21H, 7×*CH*$_3$CO); ^{13}C NMR (DMSO-d_6): δ 178.91 (C=S), 170.06–169.15 (7×C=O), 159.04 (C-4 aromatic), 150.12 (C=N), 128.36 (C-2 & C-6 aromatic), 128.05 (C-1 aromatic), 115.06 (C-3 & C-5 aromatic), 95.36 (C-1'), 80.94 (C-1), 74.33 (C-3), 73.87 (C-4), 72.87 (C-5), 71.24 (C-2), 69.53 (C-5'), 68.91 (C-3'), 67.99 (C-2'), 67.83 (C-4'), 62.90 (C-6'), 61.45 (C-6), 20.58–20.23 (7s, 21H, 7×*CH*$_3$CO), 14.20 (C=N–CH_3).

Compound 3l (R=4-OMe): ^{1}H NMR (DMSO-d_6): δ 10.70 (s, 1H, NH), 8.46 (d, 1H, *J* 9.05 Hz, NH), 7.85 (d, 2H, *J* 8.9 Hz, H-2 & H-6 aromatic), 6.94 (d, 2H, *J* 8.9 Hz, H-3 & H-5

aromatic), 5.86 (t, 1H, *J* 9.25 Hz, H-1), 5.45 (t, 1H, *J* 9.25 Hz, H-3), 5.30 (d, 1H, *J* 3.75 Hz, H-1'), 5.23 (t, 1H, *J* 9.95 Hz, H-3'), 5.14 (t, 1H, *J* 9.25 Hz, H-2), 4.98 (t, 1H, *J* 9.95 Hz, H-4'), 4.86 (dd, 1H, *J* 10.2 Hz, *J* 3.75 Hz, H-2'), 4.34 (dd, 1H, *J* 12.2 Hz, *J* 2.3 Hz, H-6a), 4.18 (dd, 1H, *J* 5.0 Hz, *J* 12.2 Hz, H-6b), 4.15 (dd, 1H, *J* 4.85 Hz, *J* 12.7 Hz, H-6'a), 4.01 (ddd, 1H, *J* 9.3 Hz, *J* 5.0 Hz, *J* 2.3 Hz, H-5), 4.00 - 9.93 (m, 3H, H-6'b, H-5', H-4), 3.79 (s, 3H, O-CH_3), 2.28 (s, 3H, C=N–CH_3), 2.04 - 1.92 (7s, 21H, 7×CH_3CO); ^{13}C NMR (DMSO-d_6): δ 179.04 (C=S), 169.91–169.01 (7×C=O), 160.47 (C-4 aromatic), 149.67 (C=N), 129.62 (C-1 aromatic), 128.17 (C-2 & C-6 aromatic), 113.59 (C-3 & C-5 aromatic), 95.28 (C-1'), 80.89 (C-1), 74.25 (C-3), 73.87 (C-4), 72.86 (C-5), 71.20 (C-2), 69.48 (C-5'), 68.87 (C-3'), 67.92 (C-2'), 67.83 (C-4'), 62.81 (C-6'), 61.40 (C-6), 55.15 (4-OCH_3), 20.46-20.12 (7s, 21H, 7×CH_3CO), 14.17 (C=N–CH_3).

III - RESULTS AND DISCUSSION

Required 2,2',3,3',4,6,6'-hepta-*O*-acetyl-β-maltosyl thiosemicarbazide was prepared in according to reference [6-8]. New substituted acetophenone (2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiosemicarbazones (**3a-l**) were obtained by condensation of corresponding thiosemicarbazide (**1**) with corresponding substituted acetophenones (**2a-l**). Reactions were performed in absolute ethanol in the presence of glacial acetic acid as catalyst using microwave-assisted method (scheme 1).



2a-l, 3a-l: H(**3a**), 4-NO_2 (**3b**), 3-NO_2 (**3c**), 3-NO_2-4-Br (**3d**), 3-NO_2-4-OMe (**3e**), 3-NO_2-4-OEt (**3f**), 4-Cl(**3g**), 4-Br (**3h**), 4-Me (**3i**), 4-OH (**3k**), 4-OMe (**3l**)

Scheme 1.

IR spectra of thiosemicarbazones **3a-l** showed characteristic absorptions in the range of 3386 - 3376

and 3338 - 3304 cm^{-1} (N–H), 1758 - 1744 (ester C=O), 1539 - 1524 and 1485 - 1400 (aromatic C=C), 1377 - 1369 (C=S), 1234 - 1223 and 1045 - 1023 cm^{-1} (ester C–O–C) and 1620 - 1602 cm^{-1} (C=N imine).

The ^{1}H-NMR spectra of substituted acetophenone 2,2',3,3',4,6,6'-hepta-*O*-acetyl-*β*-maltosyl thiosemicarbazones **3** show resonance signals at δ 1.9 - 2.1 ppm (singlet, $COCH_3$), δ 3.9–5.9 ppm (protons in pyranose ring), δ 7.0 - 8.5 ppm (aromatic protons), δ 10.7 - 10.9 ppm (singlet, NH) and δ 8.5 - 8.6 ppm (doublet, NH), δ 2.2 - 2.4 ppm (singlet, methyl-protons in N=C–CH_3 bond group). The coupling constants of H-1 and H-2 in pyranose ring are ^3J = 9.2 - 9.3 Hz indicating the H-H-*trans* relationships of these protons, i.e. thiosemicarbazones have *β*-anomeric configuration. The ^{13}C-NMR spectrum of compound **3** showed resonance signals at δ 179.4 - 179.3 ppm (carbon atom in C=S group), δ 169.9 - 169.3 ppm (carbon atoms in C=O bond of acetyl groups), δ 150.0 - 147.0 ppm (benzene ring), δ 81.3 - 61.7 ppm pyranose ring) and δ 21.5 - 21.1 ppm (methyl-carbons in acetyl groups).

Table 1: Acetophenone (2,2',3,3',4,6,6'-hepta-*O*-acetyl-β-maltosyl)-thiosemicarbazones **3**

Entry	mp, ºC	Yield, %	Solvent	IR Spectra, cm^{-1}				
				ν_{NH}	$\nu_{C=N}$	$\nu_{C=O}$	ν_{COC}	$\nu_{C=S}$
3a	165 - 166	51	Ethanol	3469, 3311	1622	1745	1233, 1045	1369
3b	199 - 200	85	Ethanol	3494, 3338	1602	1747	1232, 1041	1374
3c	164 - 165	58	Acetic acid	3477, 3307	1605	1749	1233, 1041	1373
3d	178 - 179	71	Acetic acid	3477, 3307	1611	1749	1234, 1041	1373
3e	198 - 199	65	Ethanol	3551, 3317	1620	1748	1239, 1042	1370
3f	210 - 211	75	Ethanol	3386, 3315	1622	1754	1223, 1036	1377
3g	188 - 189	45	Acetic acid	3483, 3304	1602	1746	1231, 1044	1376
3h	192 - 193	70	Ethanol	3379, 3308	1619	1758	1225, 1041	1372
3i	192 - 193	51	Ethanol	3476, 3304	1621	1744	1231, 1043	1370
3k	160 - 161	49	Ethanol	3456, 3334	1611	1749	1240, 1040	1372
3l	190 - 191	67	Ethanol	3378, 3328	1602	1744	1263, 1023	1377

The formation of thiosemicarbazones of acetophenones could be confirmed by the presence of magnetic resonance signal of imine bond in both ^{1}H NMR and ^{13}C NMR. Especially, the formation of isomeric thiosemicarbazones in case of compound with R = 4-NO_2 that could be elucidated by its NMR spectrum. The ^{1}H NMR shows signals at δ 8.30 (d, 2H, *J* 8.5 Hz, H-3 & H-5 aromatic), 8.16 (d, 2H, *J* 8.9 Hz, H-2 & H-6 aromatic), 2.38 (s, 3H, C=N–CH_3) (for compound **3b**) and at δ 8.21 (d, 2H, *J* 8.0 Hz, H-3 & H-5 aromatic), 8.17 (d, 2H, *J* 8.0 Hz, H-2 & H-6 aromatic), 2.32 (s, 3H, C=N–CH_3) (for compound **3b'**). The ^{13}C NMR shows signals at δ 156.07 (C-4 aromatic), 147.65 (C=N), 143.54 (C-1 aromatic), 127.89 (C-2 & C-6 aromatic), 123.60 (C-3 & C-5 aromatic), 15.03 (C=N–CH_3) (for compound **3b**) and at δ 148.10 (C-4 aromatic), 147.18 (C=N), 143.31 (C-1 aromatic), 127.85 (C-2 & C-6 aromatic), 123.24 (C-3 & C-5 aromatic), 14.40 (C=N–CH_3) (for compound **3b'**). Ratio of **3b** and **3b'** is 62.77% and 37.23%.

In conclusion, per-*O*-acetyl-β-maltosyl thiosemicarbazone of substituted acetophenones were synthesized and the conditions in reaction solvents were investigated.

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