NMR SPECTRA OF SOME *N*-(TETRA-*O*-ACETYL-β-D-GLYCOPYRANOSYL)THIOSEMICARBAZONES FROM NATURAL CARBONYL COMPOUNDS

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SUMMARY

PHỔ NMR CỦA MỘT SỐ *N*-(TETRA-*O*-ACETYL-β-D-GLYCOPYRANOSYL)THIOSEMICARBAZON TỪ CÁC HỢP CHẤT CARBONYL THIÊN NHIÊN

Các N-(tetra-O-acetyl-β-D-glycopyranosyl)thiosemicarbazon của một số aldehyd và keton có nguồn gốc thiên nhiên đã được tổng hợp và nghiên cứu phổ MNMR. Phổ ^{1}*H và* ^{13}*C NMR của các thiosemicarbazon này đã được thảo luận. Các tín hiệu cộng hưởng từ trong phổ NMR của chúng chỉ ra mối quan hệ giữa cấu trúc và vị trí của tín hiệu cộng hưởng. Cấu hình β của các thiosemicarbazon này được xác nhận dựa vào hằng số ghép cặp J = 9.5–8.5 Hz giữa proton NH-4 của liên kết thiosemicarbazon và proton H-1' trong hợp phần đường.*

1. INTRODUCTION

Carbonyl compounds in nature is a source of precious aromas, some of them are more notable active, such as antibacterial, antifungal, anticancer… In addition, it also has many applications in the food industry as flavoring for confectionery, perfumes. Studies on the synthesis of thiosemicarbazones from natural carbonyl compounds have not been studied much, only very few of the references mentioned in this regard [1,6]. In order to contribute to the research in the field of chemistry of monosaccharides, in this article, we have reported some results in synthesis and spectral study of some thiosemicarbazones containing monosaccharide component with some natural carbonyl compounds.

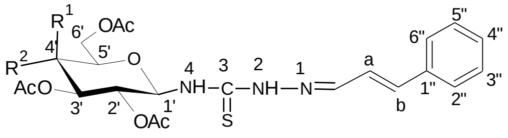
2. EXPERIMENTAL PART

N-(Tetra-*O*-acetyl-β-D-glycopyranosyl**)**thiosemicarbazides were prepared by synthetic methods in [7]. *N*-(Tetra-*O*-acetyl-β-D-glycopyranosyl)thiosemicarbazones were synthesized in bellow procedure. Their ^{1}H and ^{13}C NMR spectra was recorded on FT-NMR Avance AV500 Spectrometer (Bruker, Germany) at 500.13 MHz and 125.76 MHz, respectively, using DMSO-d_6 as solvent and TMS as an internal standard. Spectral data of ^{1}H and ^{13}C NMR were summarized in Tables 1 and 2. Aldehydes and ketones used in this article have been isolated from Vietnamese plant oils by using known common suitable methods. Cinnamaldehyde was isolated from *Cinnamomum cassia* (Bl.) oil. Menthone was prepared from menthol of *Mentha arvensis* (L.) plant. Camphor was isolated from *Cinnamomum camphora* (L.) Nees. et Eberm plant.

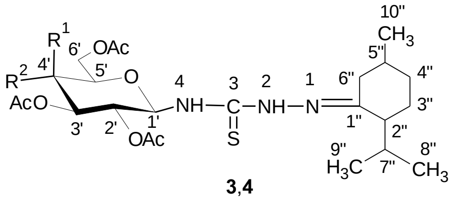
General procedure tetra-O-acetyl-β-D-glycopyranosyl thiosemicarbazones. A mixture of corresponding *N*-(tetra-O-acetyl-β-D-glycopyranosyl**)**thiosemicarbazide (2 mmol), corresponding natural carbonyl compound (2 mmol), glacial acetic acid (0.5 ml) in absolute ethanol (9 ml) was heated at reflux using domestic microwave oven in 8 min at power of 800W. The solvent was evaporated to one half the original volumes. The resulting colorless crystals were filtered by suction. The crude product when recrystallized from 96% ethanol to afford the title compounds **1**-**5**.

3. RESULTS AND DISCUSSION

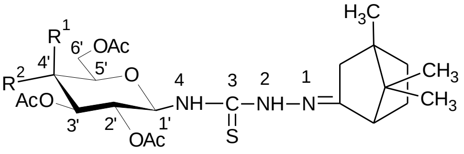
The ^{1}H and ^{13}C NMR spectral data of tetra-*O*-acetyl-β-D-glycopyranosyl thiosemicarbazones **1-5** from natural carbonyl compounds were listed in Table 1 and 2. The ^{1}H and ^{13}C NMR spectra of these thiosemicarbazones showed a distinct signal regions specified to each type of proton and carbon-13 atoms are present in molecule of the compounds. The structures of these thiosemicarbazones are represented below.



1, **2**



3,**4**



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Cinnamaldehyde peracetylated glycopyranosyl thiosemicarbazones:
1 R^1=H, R^2=OAc; **2** R^1=OAc, R^2=H

Menthone peracetylated glycopyranosyl thiosemicarbazones:
3 R^1=H, R^2=OAc; **4** R^1=OAc, R^2=H

Camphor peracetylated glycopyranosyl thiosemicarbazones:
5 R^1=H, R^2=OAc

Protons in NH-2 and NH-4 bonds in thiosemicarbazone group have signal at δ=11.94–11.89 ppm (singlet, for cinnamaldehyde thiosemicarbazones), δ=10.86–10.50 ppm (singlet, for camphor and menthone thiosemicarbazones) and δ=8.55–8.336 ppm (doublet, J=9.5–9.0 Hz, for cinnamaldehyde thiosemicarbazones) and δ=8.17–8.06 ppm (doublet, J=9.5–9.0 Hz, for camphor and menthone thiosemicarbazones), respectively. Proton of azomethin group (CH=N) shows chemical shift at δ=7.94–7.93 ppm (singlet), and carbon atom in this group has signal at about 146,0 ppm. Aromatic protons have resonance signals in region at δ=7.57–7.33 ppm (doublet, J =7.5–7.25 Hz, for cinnamaldehyde thiosemicarbazones). There are two proton signals for di-*trans*-substituted alkene appear at δ=7.07–6.95 ppm with the coupling constants J=16.00 Hz. These values of the coupling constants demonstrate the alkene combined with aromatic rings in cinnamaldehyde component has *trans*-configuration.

Protons in CH_3 group in acetate functions have signals in region at δ=2.14–1.90 ppm. Protons of monosaccharide component have signals including in range from 5.97 ppm to 3.98 ppm. The distinct structure pattern of galactopyranose ring, compared with the one of glucopyranose ring, is confirmed by coupling constant between H-4” and H-3” protons with ^3J=3.25–3.00 Hz in galactopyranose ring, compared with the coupling constant ^3J=9.75–9.25 Hz in glucopyranose ring. Protons on C-1’ and C-2’ carbon atoms in glucose and galactose ring have coupling interaction with the constants ^3J=9.5–8.5 Hz, in relation to H–H interaction of *trans* type, therefore, thiosemicarbazide linkage group is *equatorial* direction, i.e. all tetra-*O*-acetyl-β-D-glycopyranosyl thiosemicarbazones have β-anomeric configuration [4].

The ^{1}H NMR spectrum of camphor *N*-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone, for instance, shows the proton resonance signals present in the camphor component, located in the region δ=1.05–0.67 ppm, while proton resonance signals in NH-2 (δ= 10.50 ppm) shifted dramatically toward a down-field due to the anisotropic effect of the >C=S and >C=N– adjacent links, whereas the position of the proton resonance signals of NH-4 (δ=8.17ppm) only changed a little and appears as doublet at δ=8.17 ppm with the constant pairing pair ^3J=9.00 Hz.

The long-range interactions between carbon atoms and protons in the HMBC spectrum of menthone 4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazone can be described as follows:

Table 1. ^{1}H NMR Spectra data of tetra-O-acetyl-β-D-glycopyranosyl)thiosemicarbazones [δ (ppm), multicity, J (Hz)]

Proton	**Cinnamaldehyde thiosemicarbazones**		**Menthone thiosemicarbazones**		**Camphor thiosemicarbazones**
	1	**2**	**3**	**4**	**5**
NH-2	11.89(s,1H)	11.94(s,1H)	10.85(s,1H)	10.86(s,1H)	10.50(s,1H)
NH-4	8.55(d,1H,*J*9.0)	8.33(d,1H,*J*9.50)	8.07 (d,1H,*J*9.5)	8.07 (d,1H,*J*9.50)	8.17(d,1H,*J*9.0)
CH=N	7.93(d,1H,*J*9.0)	7.94(d,1H,*J*9.00)	-	-	-
CH_a	6.90(dd,1H,*J*16.0)	6.94 (dd,1H,*J*16.0)	-	-	-
CH_b	7.07 (d,1H,*J*9.5,16.0)	7.07(d,1H,*J*16.0)	-	-	-
H-1’	5.97(t,1H,*J*9.0)	5.92(t,1H,*J*9.50)	5.84 (t,1H,*J*8.75)	5.84 (t,1H,*J*9.25)	5.80(t,1H,*J*9.25)
H-2’	5.22(t,1H,*J*9.25)	5.20(t,1H,*J*9.50)	5.04 (t,1H,*J*9.5)	5.04 (t,1H,*J*9.50)	5.11(t,1H,*J*9.25)
H-3’	5.40(t,1H,*J*9.5)	5.39 (dd,1H,*J*3.25)	5.42 (t,1H,*J*9.25)	5.42 (t,1H,*J*9.50)	5.42(t,1H,*J*9.5)
H-4’	4.95(t,1H,*J*9.5)	5.19(d,1H,*J*3.00)	4.94 (t,1H,*J*9.75)	4.95 (t,1H,*J*9.50)	4.96(m,1H)
H-5’	4.06(ddd,1H,*J*2.0, 4.5,9.5)	4.04-4.03(m,2H)	4.04-4,03(m,1H)	4.07-4.02(m,1H)	4.34(d,1H,*J*9.25)
H-6’a	4.19(dd,1H,*J*4.5, 12.5)	4.32-4.34(m,1H)	4.16(dd,1H, *J*4.75,12.5)	4.16(dd,1H,*J*5.00,12.50)	4.20(dd,1H,*J*4.5, 12.75)
H-6’b	3.98(d,1H,*J*11.5)	4.04-4.03(m,2H)	3.98(d,1H, *J*2.0,12.5)	3.98(dd,1H, *J*2.00,12.25)	4.01 (d,1H,*J*2.5,12.25)
H-2”	7.57(d,2H,*J*7.5)	7.59(d,2H,*J*7.50)	(A) 3,37-0,86(m, 16H)	(B) 2,92-0,86(16H)	(C) 1,05-0,67(m,16H)
H-3”	7.40(t,2H,*J*7.25)	7.40(d,2H,*J*7.50)			

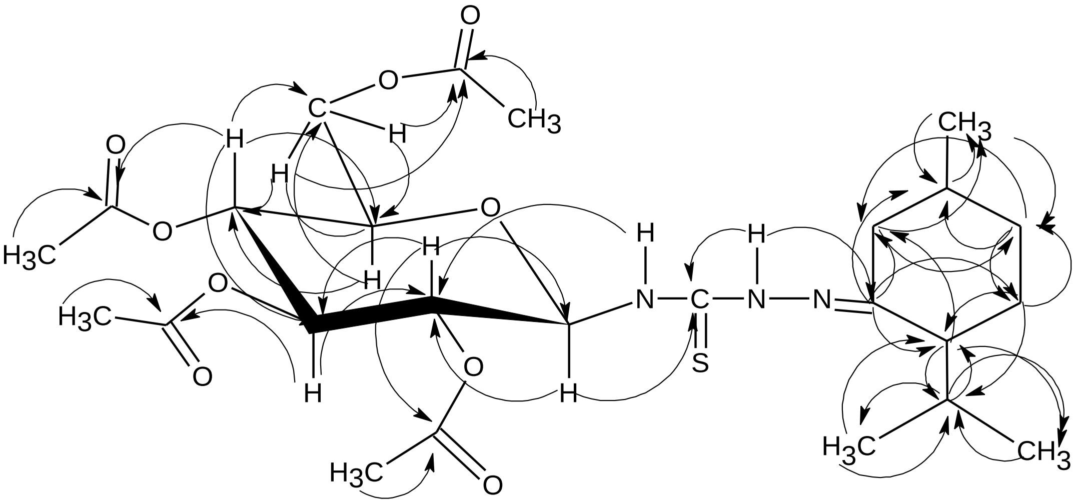
Proton	**Cinnamaldehyde thiosemicarbazones**		**Menthone thiosemicarbazones**		**Camphor thiosemicarbazones**
	1	**2**	**3**	**4**	**5**
H-4”	7.33(t,1H,*J*7.5)	7.33(t,1H,*J*7.25)	2,23-2,19 (m, 1H) 1,78-1,76 (m, 1H) 1,67-1,63 (m, 1H) 1,18-1,14 (m, 4H) 0,94-0,86 (m, 9H)	2,23-2,19 (m, 1H) 1,78-1,76 (m, 1H) 1,67-1,63 (m, 1H) 1,18-1,14 (m, 4H) 0,94-0,86 (m, 9H)	0,81(s,1H) 0,76(s,2H) 1,00(s,3H) 0,89(s, 6H) 0,71-0,67(m,4H)
H-5”	7.40(t,2H,*J*7.25)	7.40(d,2H,*J*7.50)			
H-6”	7.57(d,2H,*J*7.5)	7.59(d,2H,*J*7.50)			
CH$_3$CO	2.00-1.93(s,12H)	2.14-1.94(s,12H)	1.99-1.92	1.95-1.90(s,12H)	2.01-1.95

Note: (A), (B), (C): proton signals in methone and camphor, respectively.

Table 2. ^{13}C NMR Spectra data of N-(tetra-O-acetyl-β-D-glycopyranosyl)thiosemicarbazones

Proton	**Cinnamaldehyde thiosemicarbazones**		**Menthone thiosemicarbazones**		**Camphor thiosemicarbazones**
	1	**2**	**3**	**4**	**5**
C=S	177.9	177.9	179.1	179.1	178.6
*CO*CH$_3$	170.0-169.3	170.0-169.3	170.0-169.3	170.0-169.3	170.0-169.3
C-1’	81.3	81.3	80.8	80.8	81.0
C-2’	70.8	70.8	70.5	70.5	70.4
C-3’	72.7	72.7	72.3	72.3	72.3
C-4’	67.9	67.9	68.2	68.2	68.2
C-5’	72.3	72.3	72.1	72.1	72.1
C-6’	61.8	61.8	61.8	61.8	61.7
CHa	124.7	124.7	-	-	-
CHb	135.7	135.7	-	-	-
C-1”	140.0	140.0	160.3	160.3	168.7
C-2”	129.0	129.0	50.2	50.2	52.7
C-3”	128.9	128.9	27.8	27.8	34.8
C-4”	127.0	127.0	32.5	32.5	32.1
C-5”	128.9	128.9	33.4	33.4	47.3

Proton	Cinnamaldehyde thiosemicarbazones		Menthone thiosemicarbazones		Camphor thiosemicarbazones
	1	**2**	**3**	**4**	**5**
C-6”	129.0	129.0	35.4	35.4	47.6
CH_3CO	20.5-20.3	20.5-20.3	20.5-20.2	20.5-20.2	20.5-20.2
-CH=N-	146.0	146.0	-	-	-
$CH(CH_3)_2$	-	-	26.3; 21.7; 19.0	25.8; 21.7; 19.0	26.7; 18.9; 10.8
CH_3	-	-	21.2	21.2	18.4



4. CONCLUSIONS

The ^{1}H and ^{13}C NMR spectra of peracetyled (β-D-glycopyranosyl)thiosemicarbazones of some aldehyde and ketone from natural origin have been studied and discussed. The magnetic signals in their NMR spectra show the relationships between the structural features and positions of resonance signals in NMR spectra.

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