ANALYSIS OF NMR SPECTRA OF 3-ARYL-4-FORMYLSYDNONE 4-(TETRA-*O*-ACETYL-β-D-GLUCOPYRANOSYL)THIOSEMICARBAZONES

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TÓM TẮT

PHÂN TÍCH PHỔ NMR CỦA CÁC HỢP CHẤT 3-ARYL-4- FORMYLSYDNONE 4-(TETRA-*O*-ACETYL-β-D-GLUCOPYRANOSYL)THIOSEMICARBAZON

Phổ ^{1}H và ^{13}C NMR của các 3-aryl-4-formylsydnone 4-(tetra-O-acetyl-β-D-glucopyranosyl)thiosemicarbazon đã được thảo luận. Các tín hiệu phổ được qui kết dựa vào phổ 2D NMR COSY, HSQC và HMBC. Cấu hình anomer β của các thiosemicarbazone này được xác nhận dựa vào hằng số ghép cặp J = 9,50–9,75 Hz giữa proton H-1' và H-2' trong hợp phần glucopyranose.

INTRODUCTION

The compounds contained sydnone ring interesting in terms of chemical structure [1-3] and gives these compounds the important biological properties [4,5]. Compounds containing simultaneously carbohydrate components and sydnone ring not been studied recently. Therefore, our laboratory has focused on the integrated study of this type of compound and study the chemistry and the nature of their spectrum. The compounds of 3-aryl-4-formylsydnone 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones has been synthesized according to previously procedure using microwave-assisted method [6]. In this paper we report some reviews of the NMR spectral characteristics of these compounds and understanding with respect to their structure. There are several discussions herein about the influence of structural factors to the positions of resonance signals in their ^{1}H and ^{13}C NMR spectra of 3-aryl-4-formylsydnone 4-(tetra-*O*-

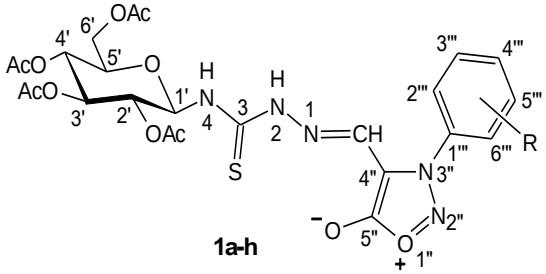
acetyl-β-D-glucopyranosyl)thiosemicarbazones.

EXPERIMENTAL PART

Substituted 3-aryl-4-formylsydnone 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones 1a-h (*Scheme 1*) were synthesized in bellow procedure [1]. 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.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR spectral data of 3-aryl-4-formylsydnone 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones 1 were listed in Tables 1 and 2. From Tables 1 and 2 it's shown that protons and carbon-13 atoms in these molecules have proper resonance signals in coresponding spectral regions which are characteristic for each atom type.



1a-h: H (**a**), 2"-Me (**b**), 3"-Me (**c**), 4"-Me (**d**), 4"-Et (**e**), 3"-OMe (**f**), 4"-OMe (**g**), 4"-OEt (**h**)

Scheme 1: Synthetic path for 4-aryl-3-formylsydnone 4-(tetra-O-acetyl-β-D-glucopyranosyl)thiosemicarbazones.

The ^{1}H NMR spectra of these thiosemicarbazones showed the characteristic resonance signals of the protons presented in molecule which are located in the region of δ=7.83–6.40 ppm for aromatic protons, δ=5.87–3.98 ppm for glucopyranose ring. Methyl groups in acetates had signals at δ=2.07–1.87 ppm (*Table 1*). The coupling constant values, $J_{H\text{-}1',H\text{-}2'}$=9.50–9.75 Hz, for the glucopyranose ring agreed with *trans*-axial H– H disposition and confirmed the β-anomeric configuration of compounds **1a-h**. The assignments of ^{1}H and ^{13}C were confirmed using COSY, HMBC and HSQC methods in case of compound **1g** (R=4'''-OMe).

The interaction of protons on neighbor carbons in molecules could be shown in ^{1}H–^{1}H COSY spectrum of compound **1g**. These interactions are in detail as follows (δ, ppm): H-2''' or H-6''' (δ 7.27) ↔ H-3''' or H-5''' (δ 7.74); NH-4 (δ 6.75) ↔ H-1' (δ 5.86) ↔ H-2' (δ 4.55) ↔ H-3' (δ 5.41) ↔ H-4' (δ 5.12) ↔ H-5' (δ 4.12-4.10) ↔ H-6'a (δ 4.27) và H-6'b (δ 4.00); H-6'a ↔ H-6'b (*Fig. 1*). The ^{13}C NMR spectral data in Table 2 showed the carbon of the aromatic ring with the signals in the δ=135.5–125.3 ppm, the carbon C-4" and C-5" of the sydnone ring has characteristic signal is in the range δ=105.6–104.6 ppm and 165.9–164.6 ppm, respectively. The carbon in the glucopyranose ring had

chemical shifts at δ=81.3–61.2 ppm. Carbon atoms in acetyl groups had signals at δ=21.5–20.1 ppm (for methyl group) and 170.5–169.2 ppm (for carbonyl group) (*Table 2*).

From the structure of thiosemicarbazones **1a-h** above we can see that in order to confirm the presence of sydnone round can not be used ^{1}H NMR spectrum, because the unique C–H bond of sydnone ring substituted by the other group. So the presence of the sydnone ring could be recognized by the presence of resonance signal lying in region at δ=105.6–104.6 ppm. The HMBC spectral results of compound **1g** showed the long-ranged interaction that appeared in spectrum. Some typical ones are below: Carbon atom C-1’ (δ=80.4 ppm) interacts with proton H-2’ (δ=4.55 ppm), carbon C-2’ (δ=70.9 ppm) with protons H-1’ (δ=5.86 ppm) and H-3’ (δ=5.41 ppm), carbon C-3’ (δ=72.1) with protons H-2’ and H-4’ (δ=5.12 ppm), carbon C-4’ with protons H-3’ and H-6’b (δ=4.00 ppm) (*Fig. 2*).

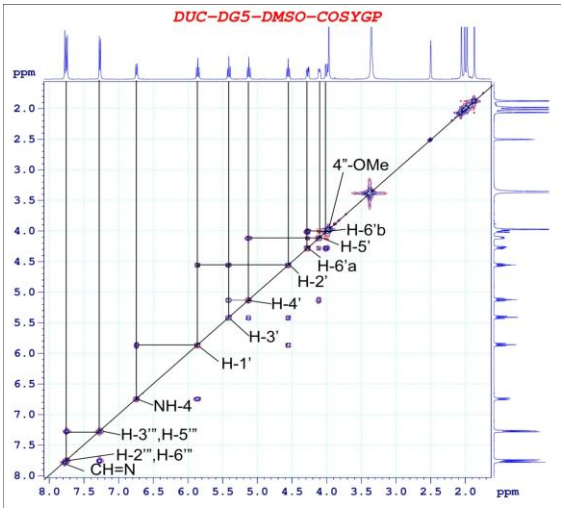


*Figure 1. COSY spectrum of thiosemicarbazone **1g** (R=4’’’-OMe).*

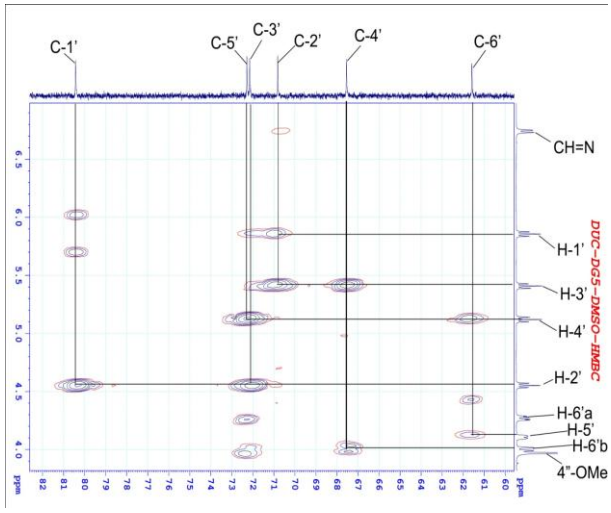


*Figure 2. HMBC spectrum (sugar region) of thiosemicarbazone **1g** (R=4’’’-OMe).*

*Table 1. ^{1}H NMR spectral data of thiosemicarbazones **1a-h** [δ (ppm), multiplicity, J (Hz)]*

Proton	H (1a)	2"'-Me (1b)	3"'-Me (1c)	4"'-Me (1d)	4"'-Et (1e)	3"'-OMe (1f)	4"'-OMe (1g)	4"'-OEt (1h)
NH-2	12.96;s;1H	12.0;s;1H	11.98;s;1H	12.04;s;1H	12.01;s;1H	11.97;s;1H	12.02;s;1H	12.04;s;1H
NH-4	7.05;d;1H;J 9.5	7.71-7.68;m;2H	7.00;d;1H;*J* 10.0	6.73;d;1H;*J* 10.0	7.08;d;1H;*J* 10.0	7.18;d;1H;*J* 9.5	6.75;d;1H;*J* 10.0	6.75;d;1H;*J* 10.0
H-1'	5.88;t;1H;*J* 9.5	5.85;t;1H;*J* 9.75	5.87;t;1H;*J* 9.5	5.85;t;1H;*J* 9.5	5.90;t;1H;*J* 9.5	5.88;t;1H;*J* 9.5	5.86;t;1H;*J* 9.75	5.88;t;1H;*J* 9.5
H-2'	4.81;t;1H;*J* 9.5	4.75;t;1H;*J* 9.25	4.72;t;1H;*J* 9.5	4.54;t;1H;*J* 9.25	4.73;t;1H;*J* 9.5	4;80;t;1H;*J* 9.5	4.55;t;1H;*J* 9.5	4.60;t;1H;*J* 9.5
H-3'	5.40;t;1H;*J* 9.5	5.40;t;1H;*J* 9.5	5.41;t;1H;*J* 9.5	5.41;t;1H;*J* 9.75	5.44;t;1H;*J* 9.5	5.42;t;1H;*J* 9.5	5.41;t;1H;*J* 9.0	5.42;t;1H;*J* 9.5
H-4'	5.02;t;1H;*J* 10.0	5.05;t;1H;*J* 10.0	5.01;t;1H;*J* 9.75	5.12;t;1H;*J* 9.75	5.00;t;1H;*J* 9.75	5.00;t;1H;*J* 9.75	5.12;t;1H;*J* 9.75	5.06;t;1H;*J* 9.5
H-5'	4.09;ddd;1H;*J* 1.75;3.75;9.75	4.1;ddd;1H;*J* 2.0;4.0;10.0	4.10;ddd;1H;*J* 2.0;4.5;10.0	4.11;ddd;1H;*J* 2.0;4.5;10.0	4.10;ddd;1H;*J* 2.0;4.5;10.0	4.10;ddd;1H;*J* 2.0;4.5;10.0	4.12-4.10;m;1H	4.10-4.07;m;1H
H-6'a	4.23;dd;1H;*J* 4.5;12.5	4.26;dd;1H;*J* 4.5;12.5	4.24;dd;1H;*J* 4.5;12.5	4.27;dd;1H;*J* 4.5;12.5	4.19;dd;1H;*J* 4.5;12.5	4.21;dd;1H;*J* 5.0;12.5	4.27;dd;1H;*J* 4.0;12.5	4.26-4.18;m;1H
H-6'b	3.99;dd;1H;*J* 1.0;12.0	3.99;d;1H;*J* 11.5	3.98;dd;1H;*J* 1.5;12.0	3.99;d;1H;*J* 12.5	3.99;dd;1H;*J* 1.5;12.5	3.99;dd;1H;*J* 1.5;12.0	4.00;d;1H;*J* 11.0	3.99;d;1H;*J* 12.5
CH=N	7.79;s;1H	7.72;s;1H	7.78;s;1H	7.70;s;1H	7.81;s;1H	7.81;s;1H	7.77;s;1H	7.78;s;1H
H-2"'	7.83-7.74;m;5H	-	7.63-7.6;m;4H	7.27;d;2H;*J* 9.0	7.58;d;2H;*J* 8.25	7.47;t;1H;*J* 2.0	7.27;d;2H;*J* 8.75	7.24;d;2H;*J* 8.75
H-3"'	7.83-7.74;m;5H	7.71-7.68;m;2H	-	7.75;d;2H;*J* 9.0	7.74;d;2H;*J* 8.25	-	7.74;d;2H;*J* 8.75	7.73;d;2H;*J* 8.75
H-4"'	7.83-7.74;m;5H	7.60-7.50;m;1H	7.63-7.6;m;4H	-	-	7.38;dd;1H;*J* 1.0;7.5	-	-
H-5"'	7.83-7.74;m;5H	7.65-7.60;m;1H	7.63-7.6;m;4H	7.75;d;2H;*J* 9.0	7.74;d;2H;*J* 8.25	7.64;t;1H;*J* 8.0	7.74;d;2H;*J* 8.75	7.73;d;2H;*J* 8.75
H-6"'	7.83-7.74;m;5H	6.50-6.40;m;1H	7.63-7.6;m;4H	7.27;d;2H;*J* 9.0	7.75;d;2H;*J* 9.0	7.34;dd;1H;*J* 2.0;7.0	7.27;d;2H;*J* 8.75	7.24;d;2H;*J* 8.75
***CH$_3$*CO**	2.06-1.90;s;12H	2.09-1.90;s;12H	2.05-1.90;s;12H	2.06-1.87;s;12H	2.04-1.91;s;12H	2.05-1.90;s;12H	2.06-1.78;s;2H	2.07-1.87;s;2H
Other Proton	-	2.21;s;3H;2"'-CH_3	2.46;s;3H;3"'-CH_3	3.97;s;3H;4"'-CH_3	2.85;q;2H;*J* 7.5;4"'-***CH$_2$*CH$_3$**;1.30;t;3H;*J* 7.5;4"'-CH_2***CH$_3$***	3.86;s;3H;3"'-OCH_3	3.97;s;3H;4"'-OCH_3	4.26-4.18;m;4H;4"'-O***CH$_2$*CH$_3$**;3.97;s;3H;4"'-OCH_2***CH$_3$***

*Table 2. ^{13}C NMR spectral data of thiosemicarbazones **3a-h** [δ (ppm)]*

^{e13}C	H (1a)	2'''-Me (1b)	3'''-Me (1c)	4'''-Me (1d)	4'''-Et (1e)	3'''-OMe (1f)	4'''-OMe (1g)	4'''-OEt (1h)
C=S	177.7	176.9	177.2	177.2	177.3	177.2	177.2	177.3
$CH_3\underline{C}O$	170.5-169.8	170.0-169.3	170.0-169.3	170.1-169.2	170.0-169.3	170.1-169.3	170.1-169.3	170.1-169.2
CH=N	130.1	128.8	129.5	129.9	129.9	129.7	129.2	129.3
C-1'	81.3	80.7	80.7	80.4	80.7	80.8	80.4	80.5
C-2'	71.3	70.9	70.9	70.8	70.9	71.0	70.9	70.7
C-3'	72.9	72.2	72.2	72.1	72.1	72.2	72.1	72.4
C-4'	68.3	67.6	67.8	67.5	67.7	67.9	67.5	67.7
C-5'	72.7	72.4	72.3	72.3	72.3	72.3	72.3	72.2
C-6'	61.2	61.7	61.7	61.6	61.4	61.8	61.6	61.6
C-4''	105.6	105.0	104.9	104.6	104.8	105.1	104.6	104.6
C-5''	165.6	165.5	165.1	165.9	165.2	164.8	165.9	165.9
C-1'''	134.4	133.6	140.2	126.8	148.5	134.8	126.9	126.6
C-2'''	126.0	126.2	122.6	115.1	125.4	111.0	115.1	115.4
C-3'''	132.8	132.3	133.9	126.9	129.1	160.0	127.0	126.9
C-4'''	132.8	128.8	129.9	161.5	131.6	117.5	161.5	161.5
C-5'''	132.8	131.6	132.9	126.9	129.1	131.0	127.0	126.9
C-6'''	126.0	127.7	125.6	115.1	125.4	118.4	115.1	115.4
$\underline{C}H_3CO$	21.0-20.6	20.5-20.2	20.7-20.16	20.5-20.1	20.6-20.2	20.5-20.2	20.5-20.1	20.5-20.2
Other C	-	20.2 (2'''-CH_3)	20.7 (3'''-CH_3)	55.8(4'''-CH_3)	28.0(4'''-***CH_2***CH_3) 15.0(4'''-CH_2***CH_3***)	55.8 (3'''-OCH_3)	55.8 (4'''-OCH_3)	64.1(4'''-O***CH_2***CH_3);14.2(4'''-OCH_2***CH_3***)

CONCLUSIONS

The ^{1}H and ^{13}C NMR spectra of 3-aryl-4-formylsydnone 4-(tetra-*O*-acetyl-β-D-glucopyranosyl)thiosemicarbazones have been studied and discussed. The values of the coupling constant *J*=9.50– 9.75 Hz between the protons H-1' and H-2 of component glucopyranose indicated that these thiosemicarbazones have β-anomeric configuration.

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NGHIÊN CỨU THIẾT KẾ PHẦN MỀM.....*(tiếp theo tr.61)*

khả năng chế tạo dụng cụ xác định nhanh COD bằng phát quang hóa học hệ $KMnO_4/ Mn^{2+}$.

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