

¹³C-NMR spectra of methyl *O*-methyl- α -*L*-rhamnopyranosides

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The ¹³C-n.m.r. spectra of all *O*-methyl derivatives of methyl α -*L*-rhamnopyranoside have been interpreted. The evaluation of α , β , and γ effects of the methoxyl groups enabled to assign the signals to the individual skeletal carbon atoms.

Были измерены спектры ¹³C-ЯМР серии *O*-метилпроизводных метил- α -*L*-рамнопиранозида. На основании обсуждения α , β и γ эффектов метоксильных групп, сигналы были отнесены к отдельным атомам углеродного скелета.

Introduction of the Fourier transform (FT) technique into ¹H- and mainly ¹³C-n.m.r. has also offered new possibilities in the structural investigation of oligo- and polysaccharides. Especially the ¹³C-n.m.r. spectroscopy can provide valuable information of localization and anomeric configuration of the glycosidic bonds in these biomaterials if the data, obtained in the investigation of suitable model compounds, are available. It has been found that the methoxyl group has a similar effect on the chemical shift of an α carbon as the pyranoid unit linked by the glycosidic bond [1]. Therefore, *O*-methylated saccharides are considered to be the most suitable models for the interpretation of the spectra of oligo- and polysaccharides.

The first knowledge in the study of ¹³C-n.m.r. spectra of *O*-methylated pyranosides has been obtained by the analysis of the spectra of inosites and their *O*-methyl derivatives [2]. The rules valid for the ¹³C chemical shifts of *O*-methylated saccharides are given in [3—5]. The α effect results in a downfield shift (7—11 p.p.m.) of the α carbon signal after methylation of the corresponding hydroxyl group. The β effect is characterized by an upfield shift (~ 1.2—4.0 p.p.m.) of the β carbon signal [6] and has been mainly studied for the equatorial methoxyl group. Less attention, however, has been devoted to the β effect of the methoxyl group in the axial position.

In this work, the ¹³C-n.m.r. spectra of the complete series of methyl *O*-methyl- α -*L*-rhamnopyranosides have been analyzed. This enabled us to study the above-mentioned effects induced by both the equatorial (C-3, C-4) and the

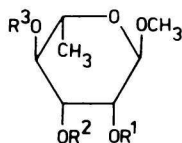
axial (C-1, C-2) methoxyl groups. The ¹H-n.m.r. spectral data of these *O*-methylated methyl α -L-rhamnopyranosides confirmed their ¹C₄ conformation [7].

For the measurements of ¹³C-n.m.r. spectra (Table 1), the following compounds were used (Scheme 1).

Table 1

¹³C-NMR chemical shifts (δ , p.p.m.) of methyl *O*-methyl- α -L-rhamnopyranosides

Compound	C-1	C-2	C-3	C-4	C-5	C-6	CH ₃ O-1	CH ₃ O-2	CH ₃ O-3	CH ₃ O-4
<i>I</i>	100.72	70.45	70.13	71.99	67.53	16.31	53.49	—	—	—
<i>II</i>	97.46	80.41	71.47	73.66	67.82	17.54	54.82	58.88	—	—
<i>III</i>	100.55	67.65	81.38	71.39	66.84	17.54	54.82	—	56.93	—
<i>IV</i>	100.71	71.31	71.07	83.25	67.09	17.87	54.74	—	—	60.67
<i>V</i>	98.37	74.99	81.16	71.67	68.18	17.77	54.87	59.09	57.06	—
<i>VI</i>	97.29	80.72	71.30	83.81	67.08	17.86	54.74	58.96	—	60.91
<i>VII</i>	100.22	67.86	81.37	81.86	67.08	17.70	54.74	—	57.50	60.75
<i>VIII</i>	97.95	77.40	81.22	82.19	67.74	17.79	54.74	59.05	57.75	60.91



	R ¹	R ²	R ³
<i>I</i>	H	H	H
<i>II</i>	CH ₃	H	H
<i>III</i>	H	CH ₃	H
<i>IV</i>	H	H	CH ₃
<i>V</i>	CH ₃	CH ₃	H
<i>VI</i>	CH ₃	H	CH ₃
<i>VII</i>	H	CH ₃	CH ₃
<i>VIII</i>	CH ₃	CH ₃	CH ₃

Scheme 1

The chemical shifts of C-1 signals were in all investigated compounds at 100.72—97.29 p.p.m. Influenced by the β effect, the C-1 chemical shifts of the compounds *II*, *V*, *VI*, and *VIII* appear \sim 3.0 p.p.m. upfield in comparison with the

C-1 signals of the compounds *I*, *III*, *IV*, *VII*, which possess the unsubstituted OH group at C-2 and are influenced by the α effect only.

The C-2 signal for compound *I* appears at 70.45 p.p.m. Due to the α effect, the C-2 signals of the compounds *II* and *VI* are shifted 9.96 and 10.27 p.p.m. downfield. The ^{13}C chemical shifts of C-2 signals of the compounds *V* and *VIII* are influenced by the prevailing α effect and the β effect with the opposite action, which results in the smaller downfield shifts (4.54 ; 6.95 p.p.m.) of these signals.

The α effect of the methoxyl group at C-3 for the compounds *III*, *V*, *VII*, and *VIII* is $\sim +11.2$ p.p.m. The C-4 signals of the compounds *IV*, *VI*, *VII* are due to the α effect shifted downfield by $\sim +11.82 - +9.87$ p.p.m. The positions of the C-5 signals in the ^{13}C -n.m.r. spectra are nearly unaffected by methylation as the *gauche* interaction between the hydrogen atoms of the methoxyl group at C-1 and the hydrogen atom at C-5 is preserved in all measured compounds.

For the compounds *II*—*VIII*, the signals of the methoxyl groups at C-1 are nearly the same. Similar observation was made for the chemical shifts at C-6. The only exception is compound *I* which was measured in CD_3OD .

The downfield shift of the C-3 signal after methylation of the hydroxyl group at C-2 is, however, unexpected, but such negative β effect has already been observed with methyl(methyl *O*-methyl- α -D-glucopyranosid)uronates [8]. The obtained data can be applied in the ^{13}C -n.m.r. structural studies of oligo- and polysaccharides, which contain L-rhamnose as the constituent sugar unit.

Experimental

The series of *O*-methylated methyl α -L-rhamnopyranosides has been prepared according to [7], where their physicochemical constants and ^1H -n.m.r. spectra are given, too.

^{13}C -N.m.r. spectra were measured at room temperature with a Jeol FX-60 instrument in CDCl_3 solutions (compounds *II*—*VIII*), except of the compound *I*, which was measured in CD_3OD . Me_4Si was used as internal standard.

The compounds *I*—*VIII* were measured using the following FT techniques: noise and off resonance decoupling with repetition time of 1 s, pulse width 4 μs (45° flip angle), 2500 Hz sweep-width (4 K real data points). An average number of accumulations was 1500 for noise decoupling and 5000 for off resonance decoupling.

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