

# Methyleneglucoses – Transition metal catalyzed synthesis from formaline and glucose; importance of heterobimetallic catalyst

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## Abstract

Iron III, ruthenium III and tin (II) chlorides catalyze the synthesis of methyleneglucoses with a yield of 13–20%. Chlorides of remaining metals and many different iron salts are considerably inferior. The yields of methyleneglucoses is further increased up to 36% when a heterobimetallic system (FeCl<sub>3</sub> + SnCl<sub>2</sub>·2H<sub>2</sub>O) is applied as a catalyst. Hypothesis of the mechanism implies formation of a heterobimetallic complex bridged by Cl, gem-diol and glucose. The structure of two methyleneglucoses was established as 1,2:5,6-di-O-methylene- $\alpha$ -glucofuranose and 1,2:3,5-di-O-methylene- $\alpha$ -glucofuranose.

**Keywords:** Catalysis; Glucose; Heterobimetallic transition metal catalyst

## 1. Introduction

Glucose is an abundant raw material. To find new reactions, with glucose, particularly catalytic, is an interesting task. We have been studying possibilities of altering the reactivity of glucose by applications of concentrated water solutions of salts as solvents [1–3]. Such systems could be useful for glucose with free hydroxyl groups. However, one can expect many catalytic transformations of glucose in not polar or slightly polar solvents – so hydroxyl should be blocked.

Acetalization with formaldehyde has some virtues: methylene acetals are the most stable to

acid hydrolysis [4]; a [–O–CH<sub>2</sub>–O–] substituent with two geminal oxygen atoms connected to a methylene moiety is promising, in our view, for further transformations; formaldehyde is a cheap C-1 chemical.

Mono and dimethyleneacetals of glucose were probably synthesized as early as in 1903 [5] by reaction of glucose with formalin in the presence of HCl or H<sub>2</sub>SO<sub>4</sub> with addition of an acetic acid. Hugh [6] claimed that he has prepared these compounds by melting glucose and paraformaldehyde in the presence of an acid catalyst.

Schmidt [7] tried to determine positions of both methylene groups attached to glucose and pronounced himself, that hydroxyls in the 1, 2, 3, 5 positions were engaged. It was pretended

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that hydroxyl in the 6th position is free also in a monomethylene derivative.

Characterization of these materials was obviously poor and uncertain.

Recently the synthesis of 1,2:3,5-di-O-methylene- $\alpha$ -D-glucofuranose was described by Nougier et al. [8] by transacetalization from dimethoxymethane catalyzed by Amberlyst 15.

However, formalin remains the cheapest and most easily available methylenating agent. This was the reason that we started to search for a catalyst for preparation of methylene acetals starting from commercial formalin. Another reason for this work was the intention to avoid proton and instead to find the simplest possible transition metal compound or system of compounds being an efficient catalyst. During this work we observed the formation of two dimethylene acetals, both existing in furanose forms. One is probably identical with that described by Nougier and it is likely that it is a thermodynamic product.

Our intention was also to obtain NMR and MS spectroscopic data in order to establish the structure firmly and to supply means for unambiguous identification of methyleneglucoses.

## 2. Experimental

### 2.1. Catalytic reaction and analysis of methyleneglucoses

Glucose (99%), formaline (37% HCHO,  $d = 1.07$ ), transition metal salts and compounds mentioned in Section 3 were commercial products used as received.

'RuSO<sub>4</sub>' was prepared according to [3]. Reactions were performed by dissolving glucose and catalyst precursor in formaline; solutions were then heated under reflux. Molar ratios and concentrations for entries 1–4 (Section 3: Results and discussion, Section 3.1: Catalytic reaction) were as follows: 0.147 mmol of catalyst precursor, 10 cm<sup>3</sup> of formaline, 8.333 mmol of glucose; gentle boiling during 24 h).

Conditions for remaining cases are specified in Tables 2 and 3. After dilution with distilled water, reacting solutions were extracted in Soxhlet with CHCl<sub>3</sub> during 6 h. Evaporation and drying to constant weight afforded a viscous oil. We made GC/MS analysis of this oil, to prepare a sample for this analysis, 0.02–0.03 g of this oil was dissolved in 2 cm<sup>3</sup> of acetone.

GC/MS was carried out with a Hewlett-Packard 5890 series II gas chromatograph combined with a 5972 mass selective detector using an Innowax capillary column. Temperature program: 35°C/30 min; 5°C/min up to 250°C; 250°C 5 min. Attempted identification of the two most abundant chromatographic peaks using the Wiley Library with a PBM search algorithm indicated a mass spectrum unknown to the library. The capillary gas chromatography of the crude product after extraction is shown in Fig. 1.

Such a gas chromatogram was observed in all extracts obtained with different catalysts. An area percent report of significant signals of one of the mixtures obtained by extraction is shown in Table 1. Area percent reports of others were similar.

Integration was performed with a chemstation integrator contained in the HP ChemStation software. Preparative separation of two di-O-methyleneglucoses was achieved by the column chromatography of the crude product on silica gel. It gave 1,2:5,6-di-O-methylene- $\alpha$ -glucofuranose A, as the first substance (elution with 7% acetone in toluene) and 1,2:3,5-di-O-methylene-

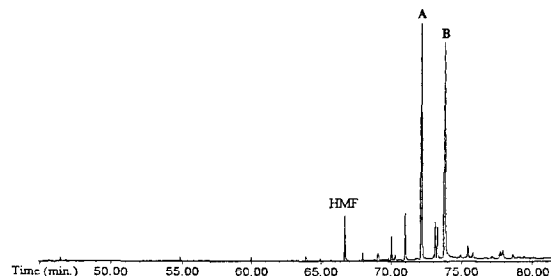


Fig. 1. Capillary gas chromatogram of crude reaction product. HMF – hydroxymethylfurfural.

Table 1  
Area percent report of signals of one of the crude extracts

Retention time (min)	Area (%)
66.68	3.96
67.96	0.70
69.04	1.14
70.04	2.16
70.30	0.63
71.00	4.43
72.18	33.54
73.12	3.64
73.30	3.54
73.85	38.26
75.43	1.61
77.70	1.15
77.89	1.66

$\alpha$ -glucofuranose B (8% acetone in toluene) as the second. Structures of these two methyleneglucosides were established by NMR and MS which is described in Section 3. The purity of both fractions was shown by capillary gas chromatography to be 98%.

## 2.2. Preparation of 'Fe[BF<sub>4</sub>]<sub>3</sub>'

Water solution of silver tetrafluoroborate has been added to the freshly prepared solution of ferric chloride in formaline under constant stirring, in room temperature. The solution has been left overnight and the next day AgCl has been filtered. No sign of metallic Ag was observed. After concentration, the solution has been used in the reaction of formaline with glucose.

## 2.3. Mass spectra

Low resolution EI mass spectra were recorded on a Hewlett-Packard 5972 mass selective detector coupled to a HP 5890 Series II gas chromatograph. The electron energy was 70 eV and the ion source temperature 170°C.

Compound A (Mw 204; m/z (rel. intensity): 201(1), 132(12), 131 (39), 115(5), 114(18), 113(4), 103(29), 102(5), 101(16), 99(4), 86(7), 85(25), 83(5), 74(5), 73(100), 72(52), 71(42),

70(4), 69(10), 68(4), 57(14), 55(10), 54(5), 45(56), 44(19), 43(28), 42(8), 41(9), 39(6).

Compound B (Mw 204); m/z (rel. intensity): 203(1), 174(3), 173(6), 144(3), 143(7), 115(11), 14(91), 113(9), 97(4), 86(7), 85(100), 84(4), 73(16), 72(23), 71(15), 69(8), 68(4), 57(22), 56(6), 55(14), 45(5), 43(13), 42(4), 41(8), 39(7).

The molecular weight of compounds A and B was confirmed using LSIMS technique on an AMD-604 double focussing mass spectrometer (AMGD Intectra GmbH, Harpsted, Germany) equipped with a 10 keV cesium gun. *m*-nitrobenzyl alcohol was used as a matrix. For both compounds, m/z = 203 (M-H)<sup>+</sup>, m/z = 205 (M + H)<sup>+</sup> and m/z = 227 (M + Na) ions were recorded.

## 2.4. NMR spectral measurements

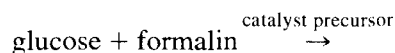
The NMR spectra were recorded on a Bruker AM 500 spectrometer in the Fourier transform mode at ambient temperatures and 0.1 M concentrations. CDCl<sub>3</sub> was used as a solvent. For NOE experiments samples were purged with helium. Chemical shifts were recorded against internal tetramethylsilane.

<sup>1</sup>H spectra were recorded with a digital resolution of 0.16 Hz/point. The MM2 calculations were performed with Hyper Chem software on a PC 486 computer. 1D <sup>1</sup>H NMR spectra were simulated using a NMRSIM program [9].

## 3. Results and discussion

### 3.1. Catalytic reaction

Reactions were performed in commercial formalin, without any additional solvent, under gentle reflux:



di-O-methyleneglucoses A and B (1)

For preliminary experiments several metal salts were selected as catalyst precursors. According

Table 2

Dependence of a yield of methyleneglucoses on composition bimetallic catalyst. Reaction conditions: 8.333 mmol of glucose; 20 cm<sup>3</sup> of commercial formaline; 24 hours of gentle boiling

Catalyst composition molar ratio	Conc. of FeCl <sub>3</sub> (10 <sup>-4</sup> M/L)	Yield of A (%)	Yield of B (%)	Yield sum total (%)
FeCl <sub>3</sub> :SnCl <sub>2</sub> · 2H <sub>2</sub> O = 1:1	7.042	19.6	12.5	32.1
FeCl <sub>3</sub> :SnCl <sub>2</sub> · 2H <sub>2</sub> O = 1:4	7.042	15.3	21.1	36.4

to the degree of conversion of glucose they can be classified into the following groups:

(1) Inactive salts: NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> · 6H<sub>2</sub>O, MnCl<sub>2</sub> · 2H<sub>2</sub>O, NiCl<sub>2</sub> · 6H<sub>2</sub>O, CoCl<sub>2</sub> · 6H<sub>2</sub>O.

(2) Iron salts and compounds giving a conversion of 0.3–7%: Fe<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub> · 9H<sub>2</sub>O, FeSO<sub>4</sub> · 7H<sub>2</sub>O, Fe[AcAc]<sub>3</sub>, Fe[OH]<sub>3</sub>, 'Fe[BF<sub>4</sub>]<sub>3</sub>', Fe<sub>2</sub>O<sub>3</sub>; a similar degree of conversion was observed with ZnCl<sub>2</sub>.

(3) Conversion of ~13–20%: FeCl<sub>3</sub> · 6H<sub>2</sub>O, RuCl<sub>3</sub> (aq.), 'RuSO<sub>4</sub>', SnCl<sub>2</sub> · 2H<sub>2</sub>O.

(4) Other salts and bicomponent systems giving conversions of ~5–15%: OsCl<sub>3</sub> (aq.), CuCl<sub>2</sub> · 2H<sub>2</sub>O, NH<sub>4</sub>Fe[SO<sub>4</sub>]<sub>2</sub> · 12H<sub>2</sub>O, FeCl<sub>3</sub> + NaCl in molar ratios (1:1)–(1:10); two salt systems in 1:1 molar ratios: ferric chloride + calcium chloride, + zinc chloride, + magnesium chloride, + aluminum chloride, + cuprous chloride, + cobalt chloride, + nickel chloride.

(5) Systems of the highest conversion described in Table 2.

The experiments described in (1)–(5) have been performed with

(a) constant concentration of a principal catalyst precursor  $1.344 \times 10^{-2}$  M/L,

(b) constant molar ratio formaline/cat. pre. ~ 8100 and glucose/cat. pre. ~ 56.

Whether there exists any dependence of the conversion on the catalyst concentration is an important point. For studying this problem we selected ferric chloride as a catalyst precursor. Results are shown in Table 3.

Increase of concentration increases conversion until a maximum ~ 32% (for a sum total of A and B); with further concentration increase, the conversion decreases.

### 3.2. Hypothesis of the reaction mechanisms

It is known that ferric chloride is a catalyst precursor for synthesis of acetals and ketals [10–12]. However, there is no information about the application of FeCl<sub>3</sub> as a catalyst for synthesis of acetals of carbohydrates. Neither corroborated mechanisms nor mechanistic hypotheses were described for any acetalization with ferric chloride. No suggestion that heterobimetallic

Table 3

Dependence of yield of methyleneglucoses on concentration of FeCl<sub>3</sub>. Reaction conditions: 8.333 mmol of glu.; 10 cm<sup>3</sup> of commercial formaline; 24 hours of gentle reflux

Conc. of FeCl <sub>3</sub> (10 <sup>-2</sup> M/L)	Molar ratio CH <sub>2</sub> O/FeCl <sub>3</sub> glu./FeCl <sub>3</sub>	Yield A (%)	Yield B (%)	Yield sum total (%)	
1.344	8100	56	10.0	10.5	20.5
2.689	4050	28	7.1	14.0	21.1
5.378	2030	14	8.5	18.7	27.2
6.722	1620	11.2	6.4	19.6	26.4
8.067	1350	9.3	7.6	25.0	32.6
9.411	1160	7.6	7.5	22.0	29.5

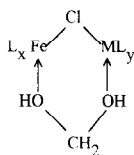


Fig. 2. Tentative structure of intermediate II formed in Eq. (2).

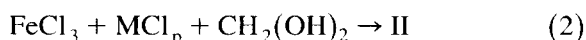
species are active has been found in the literature.

Our results, although preliminary, make an assumption that heterobimetallic species are essential for efficient catalysis likely.

The highest conversion was observed for the two metal system  $\text{FeCl}_3 + \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . An important point of interpretation is whether conversion is a result of a sum of activities of individual components or results from an activity of a new specie formed through reaction of both components. Inspection into results suggests the last possibility.

The hypothesis of the reaction mechanism is as follows:

(1) Gem diol  $\text{CH}_2(\text{OH})_2$  is a main component of the commercial formaline; it is a chelating ligand. As we observed that iron chloride is active, but iron with a noncoordinating ligand  $\text{BF}_4^-$  is completely inactive, we conclude that one of the components of the catalytic cycle –I– should be a binuclear specie with bridging Cl and  $\text{CH}_2(\text{OH})_2$ . If one deliberately works with  $\text{FeCl}_3$  and chloride of a different metal, besides I, II is formed according to Eq. (2)



The tentative structure of II is shown in Fig. 2

(2) Both compounds I and II can react with glucose. As results indicate that the heterobimetallic system is a better catalyst the further description of the reaction will be limited to the reaction path connected with compound II.

(3) In the process which follows, II reacts with glucose forming compound III shown in Fig. 3.

(4) Within this intermediate, acetalization takes place and 1,2-monomethyleneglucofuranose, water and  $\text{L}_x\text{Fe}(\text{Cl})\text{ML}_y$  are formed. This last

compound quickly reacts with formaline forming II. The catalytic cycle is therefore closed (Fig. 4).

Besides, the second cycle operates, in which a piranoside ring isomerises into furanoside. We believe, that it is carried into effect on the level of 1,2 monomethyleneglucofuranose and is catalyzed by IV. We do not intent to specify the nature of IV at present.

### 3.3. Structure of methyleneglucoses as studied by $^1\text{H}$ , $^{13}\text{C}$ NMR and MS

The only information about the structure of methyleneglucoses existing in the literature, bearing a certain degree of confidence, concerns compound B, formulated as 1,2:3,5 di-O-methylene- $\alpha$ -D-glucofuranose [8]. The authors list NMR parameters without discussion. We performed  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and MS measurements for both methyleneglucoses. We considered a discussion of the results of several NMR techniques, simulation of NMR spectra and optimization of structures by means of molecular modelling software necessary to set structural formulas possessing a satisfactory degree of certainty. They are shown in Fig. 5.

The structures concluded from our study agree with 1,2:3,5 di-O-methylene- $\alpha$ -D-glucofuranose proposed by Nougier for one, and sets 1,2:4,6 di-O-methylene- $\alpha$ -D-glucofuranose for the second.

Most of the proton chemical shifts and homonuclear coupling constants were assigned

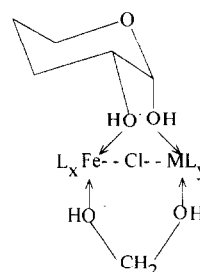


Fig. 3. Tentative structure of intermediate III formed in the reaction of II with glucose.

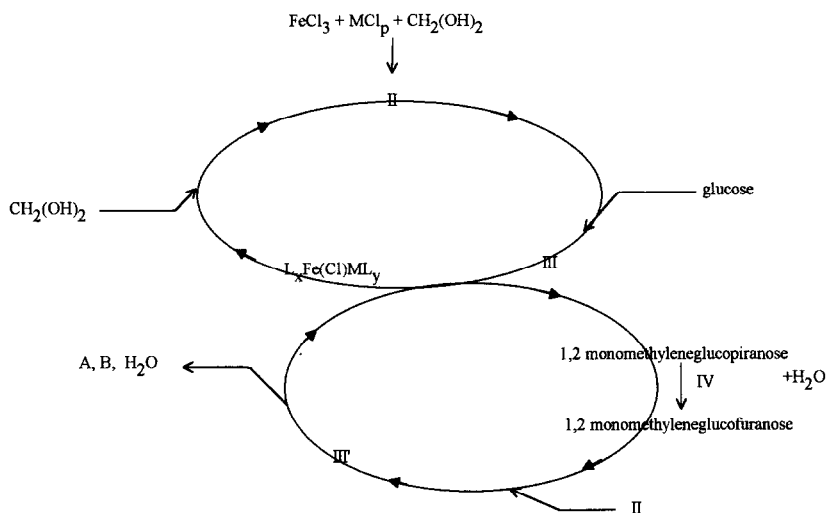


Fig. 4. Catalytic cycles operating in the system  $[\text{FeCl}_3 + \text{MCl}_p + \text{formaldehyde} + \text{glucose}]$  producing methyleneglucosides.

with the help of the  $^1\text{H}$  NMR spectra simulation program [9].

Calculated chemical shifts are listed in Table 4.

Both compounds exhibit large differences in the values of the vicinal  $^3J_{4,5}$  and geminal  $^2J_{6,6'}$  and  $^2J_{8,8'}$  coupling constants (see Table 5).

In addition, the spectra of compound B contain a set of small (ca. 0.5 Hz) long-range couplings (total multiplicities observed H-2 ddd, H-3 ddd, H-4 dd, H-5 ddddd, H-8 ddd, H-8' dd and H-1 together with lower field H-6 significantly broadened). These couplings were not observed in the proton spectrum of compound A. The geminal coupling constants for three of four methylene groups in both compounds were found to be zero, which is a typical value for protons of a methylene group adjacent to two oxygen atoms in five-membered rings [13–19]. The assignments of signals for geminal no-coupled methylene protons were done by help of the HETCOR spectra, where for each methylene group two protons from the corresponding pair connected to the same carbon atom were found. The relatively large value of the geminal  $^2J_{8,8'}$  coupling constant in the compound B suggests a different size of the ring in which the second methylene bridge is involved.

Chemical shifts in the  $^{13}\text{C}$  spectra of compounds A and B were unambiguously assigned with the help of carbon–proton HETCOR spectra. The values of carbon chemical shifts are listed in Table 6.

For three carbon signals, corresponding to atoms C-4, C-6, and C-8, a relatively large

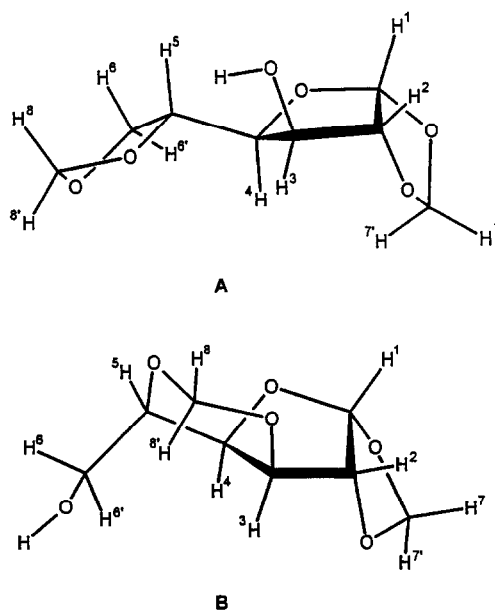


Fig. 5. Structure of the two methyleneglucosides.

Table 4  
Proton chemical shifts of dimethyleneglucooses A and B<sup>a</sup>

Compd.	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	H-7	H-7'	H-8	H-8'
A	5.94	4.43	4.38	3.95	4.2	3.99	3.98	5.05	5.00	5.03	4.81
B	6.01	4.48	4.28	3.98	4.08	3.91	3.82	5.05	5.02	4.97	4.89

<sup>a</sup> H-6, H-6', H-7, H-7' arbitrary.

Table 5  
Proton–proton coupling constants for dimethyleneglucooses A and B

compd.	<sup>3</sup> J <sub>12</sub>	<sup>3</sup> J <sub>2,3</sub>	<sup>3</sup> J <sub>3,4</sub>	<sup>3</sup> J <sub>4,5</sub>	<sup>3</sup> J <sub>5,6</sub>	<sup>3</sup> J <sub>5,6'</sub>	<sup>2</sup> J <sub>6,6'</sub>	<sup>2</sup> J <sub>7,7'</sub>	<sup>2</sup> J <sub>8,8'</sub>
A	3.7	0.7	3.1	7.9	6.5	4.9	−8.7	0.0	0.0
B	3.8	1.2	2.6	2.0	7.2	4.4	−11.6	0.0	−5.8

downfield shift (ca. 7–8 ppm) was observed for compounds A and B.

Selective INEPT via three bonds was of much help in the structure determination of both methyleneglucooses. For both compounds irradiation of the signal of the H-1 proton yielded a response from the C-4 carbon, proving that the central rings were of furanoside type in both cases. Similarly, irradiation of each of the signals of H-7 protons produced response from C-1 and C-2 carbons indicating that these carbon atoms were involved in five-membered dioxolane ring in both compounds. However, irradiation of signals of H-8 protons yielded response of the C-5 and C-6 carbons for compound A, and C-3 together with C-5 for compound B.

These results allowed us to assign the 5,6-methylene bridge involved in the dioxolane ring for compound A and 3,5 methylene bridge involved in the dioxane ring of compound B. The response to the irradiation of the signal of the H-5 proton in both cases confirmed the proposed structures. Other protons were too overlapped to suit selective irradiation.

The structural data deduced from selective INEPT measurements was subsequently refined

with the help of the analysis of proton–proton couplings. The furanoside ring fused with the dioxolane ring, possess rather little conformational freedom. Small values of vicinal  $J_{1,2}$  and  $J_{3,4}$  couplings and a small value of vicinal  $J_{2,3}$  coupling for both compounds are indicative of an envelope conformation of the furanoside ring. A large value of vicinal  $J_{4,5}$  coupling observed for compound A showed that the third ring accepts *trans* orientation across the C-4–C-5 bond in respect to the furanoside ring. The small value of that coupling for compound B indicates that the fused dioxane ring exists in chair conformation.

The significant downfield shift of the C-4, C-6 and C-8 carbon chemical shifts in the spectra of compound A in respect to the corresponding values in the spectra of compound B may be explained by stronger shielding effects of oxygen atoms, which is expected for compound A.

Additional indication of existence of conformational constraints came from NOE effects measured by NOE difference spectra, in which irradiation was performed for most of the signals. Apart of a large number of trivial effects observed for geminal and vicinal pair of protons, several non-trivial effects were also measured. For compound A a through space contact between proton H-4 and one of the H-7 protons was concluded because of the 5–6% NOE effect observed. This allowed us to assign the upper field H-7 signal to this proton and to assign an envelope conformation to the dioxolane ring

Table 6  
Carbon chemical shifts of dimethyleneglucooses A and B

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
A	104.7	85.2	75.0	82.8	72.6	68.3	96.3	95.3
B	104.4	83.6	76.5	75.6	73.2	61.7	96.5	87.2

with the methylene group located above the plane formed by four other ring atoms (see Fig. 5). One of the H-8 protons gave ca. 2% NOE effect with one of the H-6 protons and 1.5% with the H-5 proton. Another H-8 proton showed 1.5% effect with the H-4 proton. This allowed us to assign lower and higher field signals to H-8 and H-8' protons, respectively. The detailed conformation of the third ring (dioxolane) cannot be established from the measured data.

For the compound A no NOE effect was observed between H-4 and H-7 protons suggesting more expanded conformation for that part of the molecule originating from the third ring restrictions.

Lower field H-8 protons yielded quite strong, 7–9% effect with the H-3 proton; and a weaker, 3% effect with lower field H-6 protons. Higher field H-8 protons yielded a weak, 1–2% effect with the H-5 protons. This result allowed us to assign upper field to H-8 and lower field signals to H-8' protons. It also provides an indication that the dioxane ring exists in two, boat and chair, conformations.

The geometries of compounds A and B were optimized using the PCMODEL molecular modelling software, which is based on the MMX force field [20]. The optimized structures are presented on Fig. 5. Calculated coupling constants between pairs of vicinal protons (using modified Karplus equation [9]) fit well to the experimental values. It was found, that the 5-membered dioxolane rings and 6-membered dioxane ring in molecules A and B are quite flexible, therefore the large number of conformations with energies close to the minimum were found.

#### 3.4. Conclusions concerning catalytic reaction

The most active is the system, where a chance to form a heterobinuclear complex exists. The one component-atom of this complex, Fe(III) has great affinity for ligands that coordinate by oxygen [21]. One of the reactants is always a 1,1-dihydroxy compound but the second is ei-

ther 1,2 or a dihydroxy fragment where two hydroxyls are still further away. We presume that the existence of two different metals in a catalyst is essential for facilitating reactivity of 1,2 or 1,...*n* dihydroxy fragments of glucose.

Two methylene glucoses are formed in approximately equal quantities. Whether or not mono-O-methyleneglucose is formed it would be present in much smaller amounts. It indicates that catalytic species are exceptionally keen to 'exploit' as many hydroxyl groups of carbohydrate as possible. The corroborated description of mechanism of this reaction should include interaction of a metal complex with carbohydrate and with a hydrated form of formaldehyde  $\text{CH}_2(\text{OH})_2$  that constitutes the coordination chemistry of polyols. However, the detailed understanding of this chemistry is slow and difficult [22].

#### 3.5. Conclusions concerning NMR spectral studies

The full assignments of signals in proton and carbon spectra of compounds A and B was performed and the structures and favorable conformations of both dimethyleneglucoses in solution were determined. It was shown that dimethyleneglucose A consists of three five-membered rings. The furanoside ring is formed by a 1,4 connection, the dioxolane ring is closed by a 1,2-methylene bridge and another dioxolane ring is closed by a 5,6-methylene bridge. The first two rings are fused. The third ring is linked with them via a C-4–C-5 bond which exists in *trans* conformation. The furanoside ring exists in an envelope conformation. Similarly, the first dioxolane ring formed by 1,2-dimethylene bridge adopts the envelope conformation while conformation of the second dioxolane ring was not established. The conformation around the C-4–C-5 bond is the *trans* one in respect to H4 and H5 atoms.

Dimethyleneglucose B consists of three fused rings. As in A, two of them are five-membered furanoside and dioxolane rings while the third



ring is a six-membered dioxane ring. The third ring is an envelope while dioxane ring exists in two conformations, boat and preferably chair.

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