EFFECT OF Ni-Al ALLOYS ACTION ON SOME NATURAL COMPOUNDS

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Scopul acestei lucrări este de a identifica transformările care au loc la tratarea unor uleiuri vegetale şi carbohidraţi cu aliaj Ni-Al în mediu alcalin. În cazul uleiurilor, interesează determinarea capacitatăţii de reducere a legăturilor duble carbon-carbon izolate, iar în cazul carbohidraţilor se urmăreşte distingerea posibilităţii de reducere a diferiţilor acetali cu inel de cinci sau de şase atomi. În urma analizei ^{1}H-RMN s-a constatat că gradul de nesaturare al uleiurilor nu variază în urma reacţiei cu aliaj Ni-Al în soluţie NaOH, în timp ce glucoza se reduce total la sorbitol, iar zaharoza suferă o deschidere de ciclu la nivelul nucleului furanozic prin scindarea legăturii carbon-oxigen.

The purpose of this paper is to identify changes that occur during the treatment of vegetable oils and carbohydrates with Ni-Al alloy in alkaline medium. The interest was for oils to determine its ability to reduce carbon-carbon double isolated bonds, and for carbohydrates the possibility of reducing various acetals with five or six ring atoms. Following the ^{1}H-NMR analysis, it was found that degree of unsaturation of the oils does not vary after the reaction with Ni-Al alloy in NaOH solution, while glucose is completely reduced at sorbitol and the sucrose suffers a ring-opening by cleavage of furanosic carbon-oxygen bond.

Keywords: Ni-Al alloys, vegetable oils, carbohydrates, ^{1}H-NMR, chemometry

1. Introduction

Until now researches have shown that Ni-Al alloys in an alkaline medium are efficient reducing agents used to reduce multiple bonds and to cleavage bonds type C-O, C-N, C-S, C-halogen [1-3]. Our previous researches [4-6] have

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demonstrated the possibility of reducing carbon-carbon double bonds conjugated in carbonyl compounds, and facile dehalogenation of aromatic halides.

Our propose is to investigate the possibility of the reduction of carbon-carbon isolated double bonds of fatty acids from vegetable oil molecules, in the presence of Ni-Al alloy powder in an alkali medium. Using ^{1}H-NMR spectroscopy, we can obtain information of the structure and composition of the oils before and after reaction with Ni-Al alloy. We chose this analysis method because it is nondestructive and doesn't require special conditions or chemical transformation prior to analysis, as in the case of chromatographic methods [7].

The reduction of D-glucose to D-sorbitol with Raney Ni and hydrogen molecular method used on an industrial scale it is well known [8-9]. Considering that the reducing system Ni-Al alloy in basic medium can produce such hydrogenation reactions of multiple bonds and cleavage of certain simple bons [2], we aimed to investigate the behavior of the carbohydrates in this reducing system. We considered the possibility of reducing reaction of glucose to hexitol and cleavage of carbon-oxygen bonds in saccharose.

2. Materials and methods

Vegetable oils were extracted by Soxhlet standard protocol [10] from oilseeds obtained from different Romanian agricultural research stations. Glucose and saccharose are commercially available.

All reactions with oils were performed by the following procedure: in two-necked flask equipped with condenser, magnetic stirrer and dropping funnel are placed 2 g oil, 5 mL dioxane for solubilization and Ni-Al alloy 1.6 g (30 mmol Al). Over this mixture are dripped 20 mL of 20% aq. NaOH. The reaction mixture is maintained at 90°C for 9 hours, then diluted with 10 mL water and acidified with HCl until the pH becomes acidic. The mixture was extracted with 3x15 mL chloroform and the solvent was evaporated by distillation in a rotavapor at 70° C and atmospheric pressure.

Reduction of glucose occurs in the following experimental protocols: 900 mg glucose (5mmol) was dissolved in 2 mL water. This solution was placed in a round bottom flask with 360 mg Ni-Al alloy (6.75 mmol Al). Over this mixture were dropped 4.5 mL 20% aq. NaOH. The reaction mixture is maintained over stirring for 6 hours at room temperature. The next step was to neutralize the solution with HCl and to concentrate under vacuum at low temperature.

The reaction products were analyzed by ^{1}H-NMR.

^{1}H-NMR spectra were recorded on a Varian INOVA 400 spectrometer, operating at 9.4 Tesla, corresponding to the resonance frequency of 399.95 MHz for the ^{1}H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis. Samples were analyzed in 5 mm NMR tubes (Norell

507). Typical parameters for ^{1}H-NMR spectra were: 45° pulse, 2.05 s acquisition times, 6.4 KHz spectral window, 32 scans, 26 K data points and relaxation delay time 2s. The FID was not processed prior to Fourier transformation. The average acquisition time of the ^{1}H-NMR spectra was approximately 2 minutes. The NMR samples were prepared by dissolving 0.2 mL oil in 0.8 mL $CDCl_3$. The chemical shifths are reported in ppm, using the TMS as internal standard.

3. Results and discussion

3.1. Action of Ni-Al/NaOH on vegetable oils

The five types of oils: sunflower, linseed, soybean, corn and rapeseed were treated one by one with Ni-Al alloy and 20% aq. NaOH. The ^{1}H-NMR spectra of oils were compared before and after the reaction. Detailed analysis of the double bond region in the ^{1}H-NMR spectrum of vegetable oils allowed to reveal that reduction reactions occurs by lowering the intensity of signals (protons allyl bis-allyl and vinyl) [11]. For example, Fig. 1 shows the ^{1}H-NMR spectrum of the initial soybean oil.

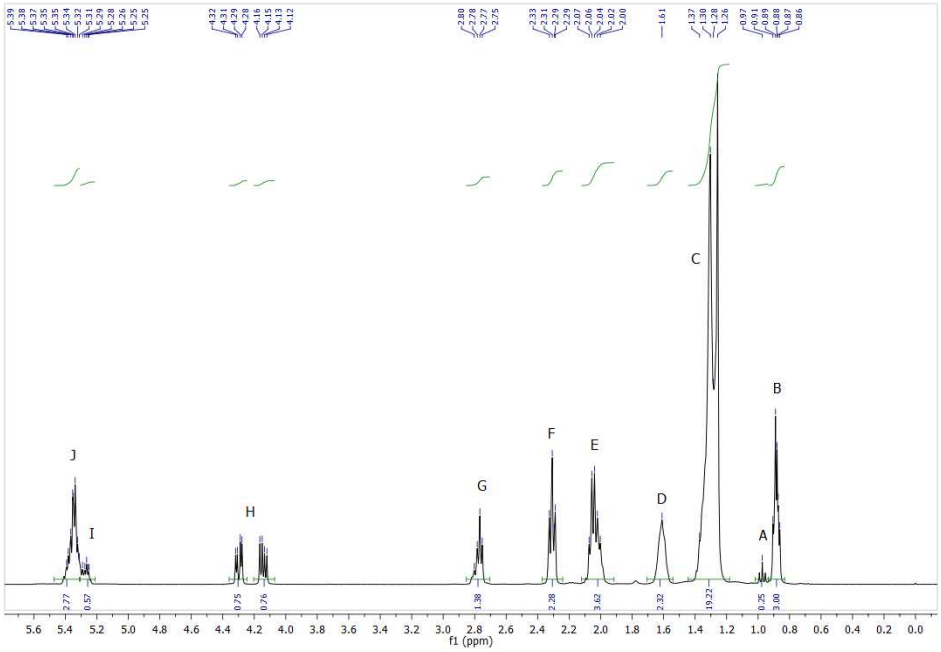


Fig. 1. ^{1}H-NMR spectrum of the soybean oil

The position of protons signals in fatty acids depends on neighboring of other functional groups. Some functional groups appear in the spectrum as

characteristic regions without overlapping the other signals, while there are other groups that have very close or overlapping signals. However, based on literature data [12] can be made an attribution of chemical shifts for functional groups (Table 1) existing in the ^{1}H-NMR spectrum of soybean oil presented earlier in figure 1. Thus, ^{1}H-NMR spectrum of oils has allowed the calculation the parameter - unsaturation degree of the lipid chains [13].

Table 1.

Chemical shifts and peak assignment of ^{1}H-RMN spectra of oils

Signal	δ (ppm)	Proton	Compound
A	0.95	-CH=CH-CH_2-C***H*****$_3$**	linolenic acid
B	0.85	-CH_2-CH_2-CH_2-C***H*****$_3$**	all acids except linolenic acid
C	1.25	-(C***H*****$_2$**)n-	all fatty acids
D	1.6	-C***H*****$_2$**-CH_2-COOH	all fatty acids
E	2.02	-C***H*****$_2$**-CH=CH-	all unsaturated fatty acids
F	2.3	-C***H*****$_2$**-COOH	all fatty acids
G	2.75	-CH=CH-C***H*****$_2$**-CH=CH-	linolic acid and linolenic acid
H	4.19	-C***H*****$_2$**-OCOR	all fatty acids
I	5.26	-C***H***-OCOR	all fatty acids
J	5.35	-C***H***=C***H***-	all unsaturated fatty acids

Fig. 2 shows the ^{1}H-NMR spectrum of soybean oil after the treatment with Ni-Al/NaOH.

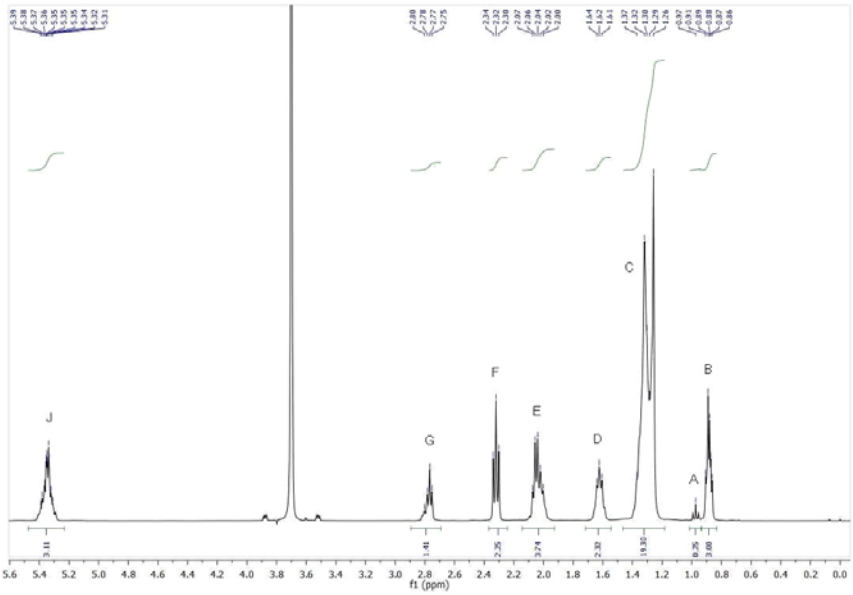


Fig. 2. ^{1}H-NMR spectrum of the soybean oil after the treatment with Ni-Al/NaOH

It was noted that in Fig. 2 do not arise signals **H** and **I** specific for protons of glycerol, because in an alkaline medium the saponification of triglycerides occurred. So, ^{1}H-NMR spectrum was now attributed to fatty acids coming from soybean oil, susceptible to be reduced in the presence of Ni-Al alloy.

The calculation of unsaturation degree shall be based on integral values of the corresponding signals in ^{1}H-NMR spectrum of the oil [14]. By a comparison between the unsaturation degrees of the oil before and after treatment with Ni-Al/NaOH we can tell if the reduction reaction occurred.

The following notations are made: I_A, I_B, I_C ... I_I and I_J – integral values of the corresponding signals **A**, **B**, **C** ... **I** and **J**.

A complication for ^{1}H-NMR spectrum of triglycerides is that signals **I** (the proton in the β position of glycerol) and **J** (protons of the group –HC=CH–) appear superposed, which does not allow separate integration. The sum of integrals **I** and **J** corresponds to $\boldsymbol{I_{I+J}}$ value. However, the integral value of signal **I** can be calculated from the balance of protons to be equal to $I_H/4$ (equation 1). Thus, the integral net signal **J** was calculated as the difference by I_{I+J} (equation 2).

$$I_I = \frac{I_H}{4} \tag{1}$$

$$I_{Jnet} = I_{I+J} - \frac{I_H}{4} \tag{2}$$

The equivalent unsaturation is obtained by using equation (3).

$$NE = \frac{3I_{Jnet}}{2(I_A + I_B)} \tag{3}$$

By using equations (1) to (3) it could be calculated the integral net value of unsaturated protons I_{Jnet} and equivalent unsaturation NE (Table 2) for five types of oil, before and after treatment with Ni-Al alloy in NaOH solution.

Table 2.

^{1}H-NMR results of the five vegetable oils analyzed

Vegetable oil sample		Integral values of CH_3 groups			Integral CH_2 glycerine	Integral values of unsaturated protons + CH		Equivalent unsaturation	Standard deviation
		I_A	I_B	I_{A+B}	I_H	I_{I+J}	I_{Jnet}		
Sunflower	initial	0.00	3.00	3.00	1.43	3.21	2.85	1.43	+0.4%
	final	0.00	3.00	3.00	0.00	2.84	2.84	1.42	-0.4%
Linseed	initial	3.25	3.00	6.25	2.97	9.12	8.38	2.01	-1.2%
	final	3.25	3.00	6.25	0.00	8.61	8.61	2.06	+1.2%
Soybean	initial	0.26	3.00	3.26	1.53	3.45	3.07	1.41	-2.7%
	final	0.25	3.00	3.25	0.00	3.23	3.23	1.49	+2.7%
Corn	initial	0.08	3.00	3.08	1.38	3.10	2.76	1.34	-0.2%
	final	0.09	3.00	3.09	0.00	2.77	2.77	1.34	+0,2%
Rapeseed	initial	0.37	3.00	3.37	1.54	3.26	2.87	1.28	+3.2%
	final	0.27	3.00	3.27	0.00	2.62	2.62	1.20	-3.2%

By analyzing the equivalent unsaturation for all the oil samples before and after the treatment with Ni-Al/NaOH it was found that both values did not vary at all. This means that the reduction reaction of C=C double bonds of fatty acid molecules has not occurred. The explanation may consist on one hand in absence of electronic effects on the C=C isolated bonds in fatty acids molecule and on the other hand in difficulty of steric matching of the large chains fatty acids with a microporous surface of Ni-Al alloy.

3.2. Action of Ni-Al/NaOH on glucose

Glucose used as starting material was characterized by ^{1}H-NMR and the signals were attributed as shown in Fig. 3. Based on NMR data it was calculated the content of α-anomer of glucose in the starting material is 88%. The product of reaction with Ni-Al/NaOH was also analyzed by ^{1}H-NMR (Fig. 4). Following the interpretation of both spectra shows that glucose was completely reduced to sorbitol.

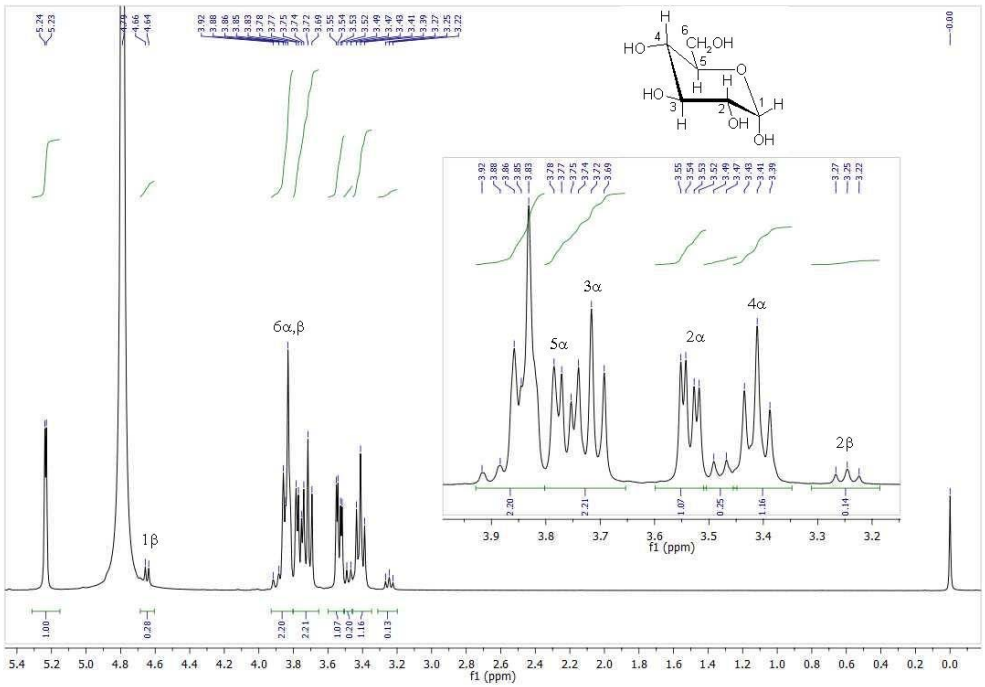


Fig. 3. ^{1}H-NMR spectrum of the glucose as starting material

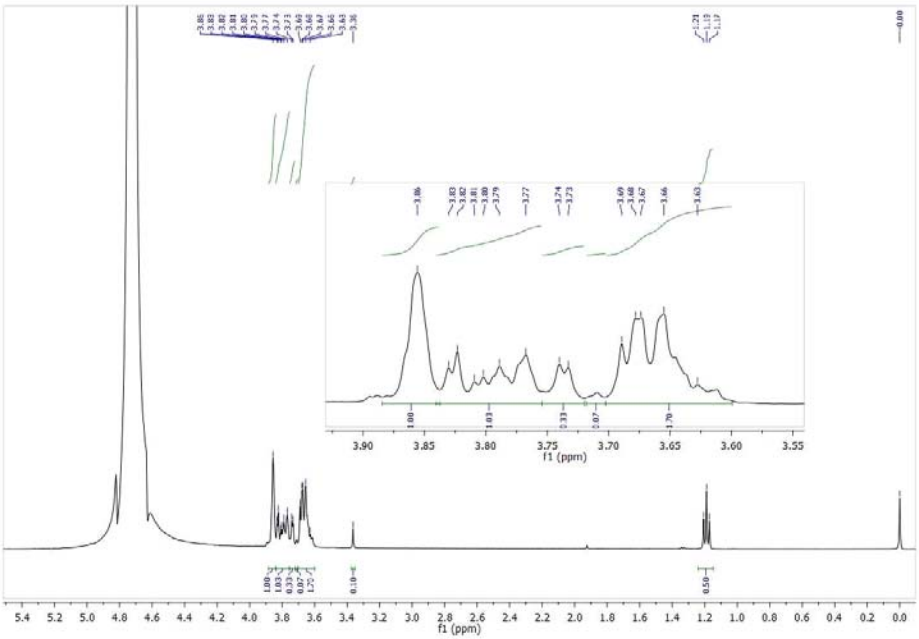
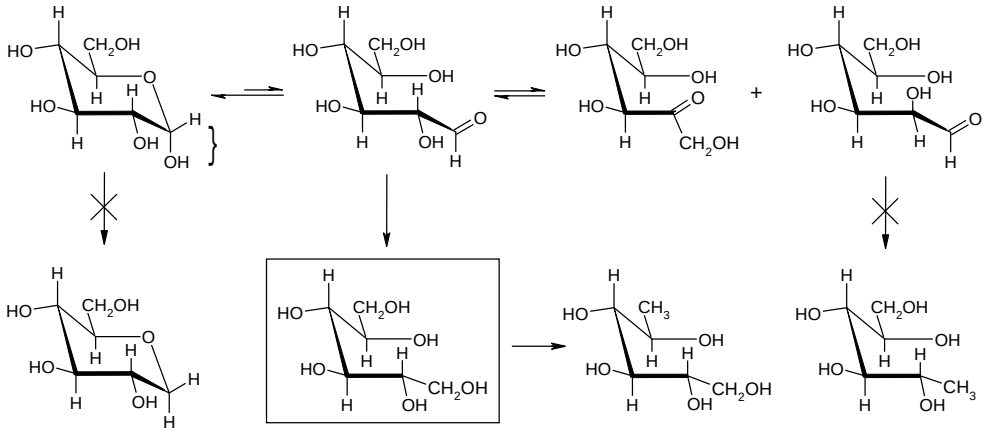


Fig. 4. ^{1}H-NMR spectrum of the glucose after the treatment with Ni-Al/NaOH

A representation of the possible transformations of glucose (Scheme 1) proposes to explain how the sorbitol formation occurs. It was noticed that the only pattern to achieve sorbitol was by reducing to alcohol of the carbonyl group in acyclic-glucose. Cyclic-glucose cannot get a reduction reaction.



Scheme 1. Reduction of glucose

3.3. Action of Ni-Al/NaOD-D_2O on saccharose

As in the case described above, it was characterized by ^{1}H-NMR sucrose as starting material (Fig. 5, Table 3) and the product obtained by reduction with Ni-Al alloy in NaOD-D_2O medium (Fig. 6).

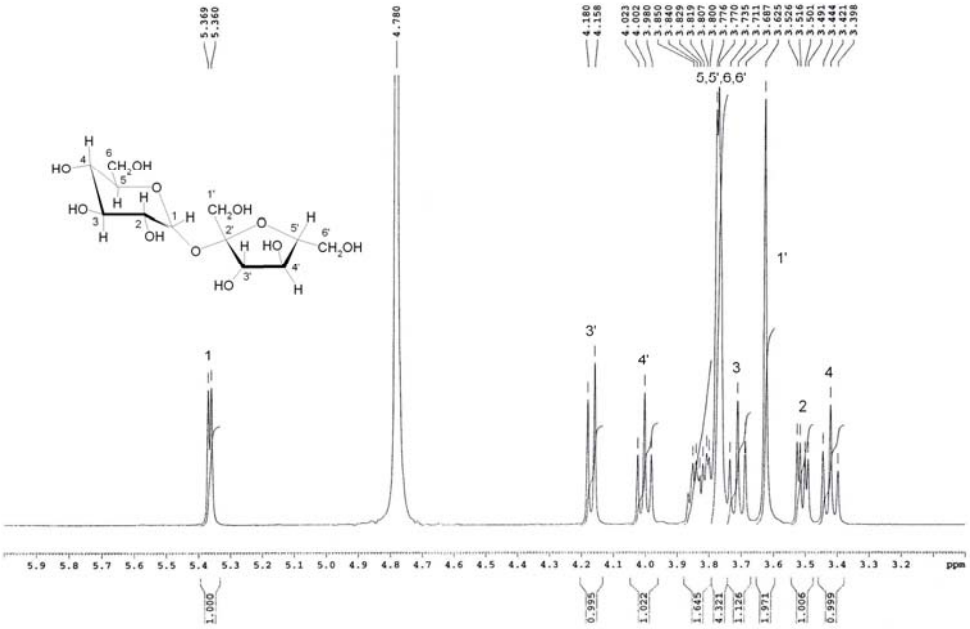


Fig. 5. ^{1}H-NMR spectrum of the saccharose

Table 3

Chemical shifts and peak assignment of ^{1}H-RMN spectra of saccharose

Signal	Number of protons	δ, ppm	Type of signal	Coupling constant
4	1H	3.42	t	J=9.2 Hz
2	1H	3.51	dd	J_1=4 Hz, J_2=9.6 Hz
1’	2H	3.63	s	-
3	1H	3.71	t	J=9.6 Hz
6+6’	4H	3.77	s	-
5+5’	2H	3.78	s	-
4’	1H	4.00	t	J=8.8 Hz
3’	1H	4.17	d	J=8.8 Hz
1	1H	5.365	d	J=4Hz

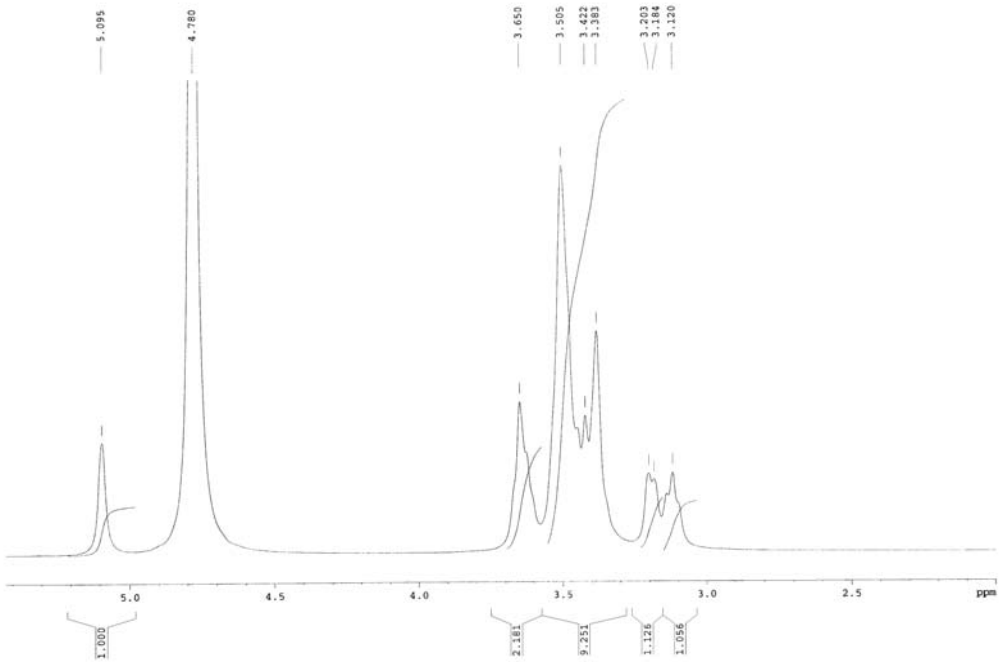
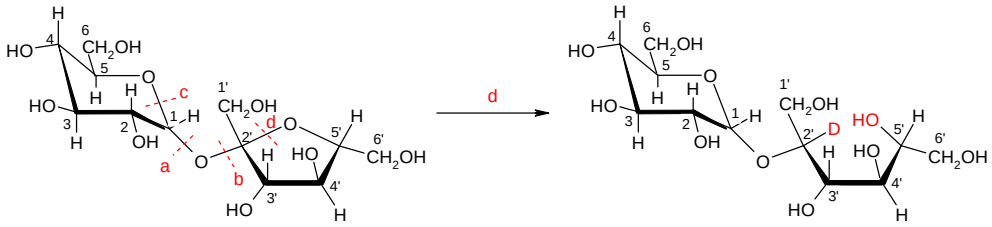


Fig. 6. ^{1}H-NMR spectrum of the saccharose after the treatment with Ni-Al/NaOD-D_2O

It was noticed that a signal appeared at 3.92 ppm instead of the combination of doublet (4.17 ppm) and triplet (4.00 ppm) corresponding to protons $H^{3'}$ and $H^{4'}$ in the fructose furanosic ring. This means that their proximity is changing and this can be explained only by cleavage of bond $C^{2'}$-O with formation of bond $C^{2'}$-D. So, there is a ring-opening in the furanosic ring of fructose.



Scheme 2. Cleavage of C-O bond in saccharose during the treatment with Ni-Al/NaOD-D_2O

So, the behavior of saccharose confirms that glucose is not reduced. The cyclic hemiacetal form of glucose does not allow the reduction reaction; the pyranosic ring remaining inert to the action of Ni-Al alloy in alkaline medium.

4. Conclusions

1) Carbon-carbon isolated double bonds from vegetable oils do not give any reduction reaction in the presence of Ni-Al alloy powder in 20% aq. NaOH, even at high temperatures.
2) The acyclic form of glucose can be easily and completely reduced to sorbitol in a reducing Ni-Al/NaOH system, while the pyranosic form is inert.
3) In case of saccharose there is a ring-opening by the cleavage of $C^{2'}$-O bond in the furanosic ring of fructose. It proved that the pyranosic ring of glucose is stable to the Ni-Al/NaOH action.

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