A. CHOSTENKO[1], S. TRUSZKOWSKI[1], A. BUCHALSKI[1], A. CHURKIN[2]

INFLUENCE OF γ–IRRADIATION ON L– AND D–MONOSACCHARIDES

Summary

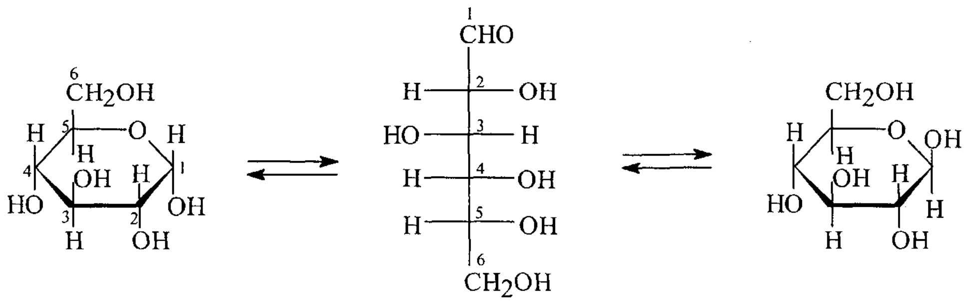
The influence of γ–irradiation on D– and L–glucose, D– and L–galactose, D– and L–mannose was examined in the solid polycrystalline state. Hydrogen was the principal gas product of radiolysis of hexoses. Radiation yield (G) of H_2 changed from 2.2 for galactose to 3.2 (1/100 eV) for glucose and mannose. The ESR spectra of radicals formed in irradiated hexoses were similar and indicated the presence of secondary radical mixture. Integral G-value of radicals decreased with dose. Process of radical disappearance could be described with equations of polychronic kinetics. Radiation stability of galactose was one and a half times higher, than radiation stability of glucose and mannose. This fact rationalised essential contribution of the C_4–H bond breaking process in formation of radical products and H_2. Radiation stability of D– and L–isomers of monosaccharides under non-polarised irradiation was identical. Radicals formed in irradiated monosaccharides lived at room temperatures for several months and it should be taken into account on application of radiation-sterilized pills.

Introduction

Radiolysis of carbohydrates in general and monosaccharides in particular always presents certain scientific interest. Sterilization of medicines in a number of countries is mainly conducted by means of radiating methods. Bearers of pill-forms consist usually of carbohydrates. A large amount of long-life radicals accumulate in carbohydrates at sterilization doses (up to 50 kGy). It can be dangerous for the users of these pills. On the other hand, a high number of isomeric forms of carbohydrates provides study of the axial and equatorial C–H bonds reactivity. The availability of L– and D–isomers gives a chance to check experimentally the hypothesis of enantiomeric excess origin under the influence of polarising radiation on saccharides.

It is known, that pyranoses can exist in one of three forms (D–glucose, as an example):

[1] *Copernicus University, Toruń, ul. Gagarina 13 Poland;* [2] *Mendeleev University, Moscow, Russia*



(1)

α–D–glucose D–glucose β–D–glucose

In aqueous solution mutarotation generates predominanly the β-form. There are 8 α-D, 8 β-D, 8 α-L, 8 β-L isomers of pyranoses and 16 linear isomers, however, the latter are of a little importance (< 1%). Crystalline forms of pyranoses had been studied showing that angles between bonds only slightly deviate from tetrahedral [1].

Radiolysis of glucose has been widely studied in various phases (polycrystalline, frozen solutions, syrups) [2–5].

Materials and methods

Irradiations of preliminary evacuated samples of hexapyranoses ("Fluka" > 99%) were performed at 25°C using a ^{60}Co source. Dose rates determined by a Fricke dosimeter were 0.25 and 2.4 kGy/h. The analysis of products was carried out on the chromatograph "Chromatron" GCHF–18.3 with a block for the analysis of gas-products (column: 3m x 4mm, carbon activated 35/50 mesh ASTM, carrier gas – N_2, heat conductivity detector).

The ESR spectra were recorded on PS/X–70 spectrometer system after irradiation immediately and in post-effect. The process of radical disappearance was investigated at 50–130°C.

Results and discussion

Hydrogen was the principal gas product of radiolysis of hexoses. Radiation chemical yield of other products was below 3% of the H_2 yield. For all hexoses the concentration of H_2 increased linearly with the applied dose (Figure 1–3). Small inductive period could be observed only in case of D–glucose. The radiation chemical yield (G-value) of H_2 changed from 2.2 for galactose to 3.2 for glucose and mannose (Table 1).

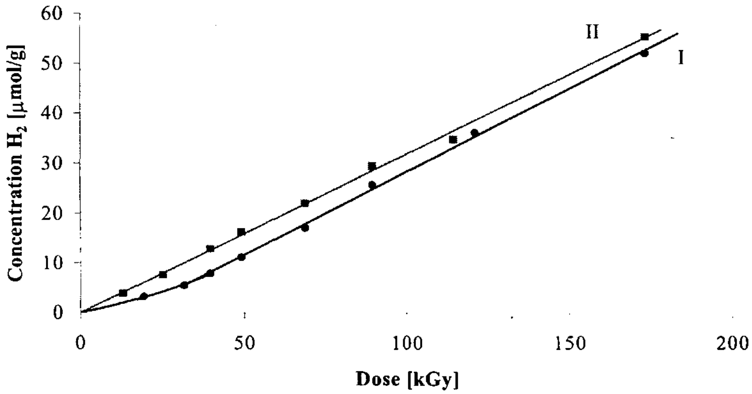


Fig. 1. Hydrogen concentration vs. the absorbed dose: I — D–glucose, II — L–glucose.

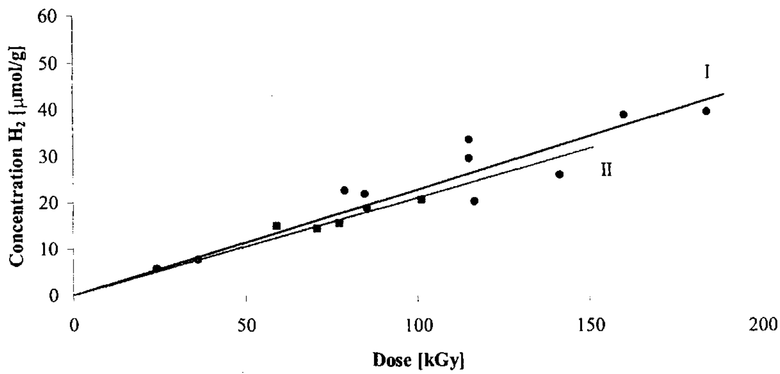


Fig. 2. Hydrogen concentration vs. the absorbed dose: I — D–galactose, II — L–galactose.

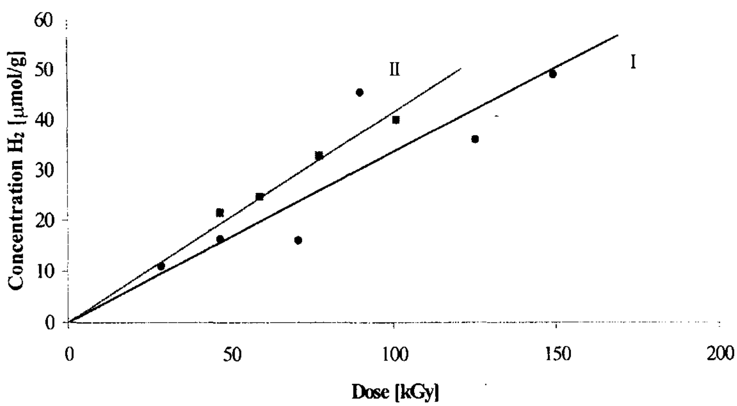


Fig. 3. Hydrogen concentration vs. the absorbed dose: I — D–mannose, II — L–mannose.

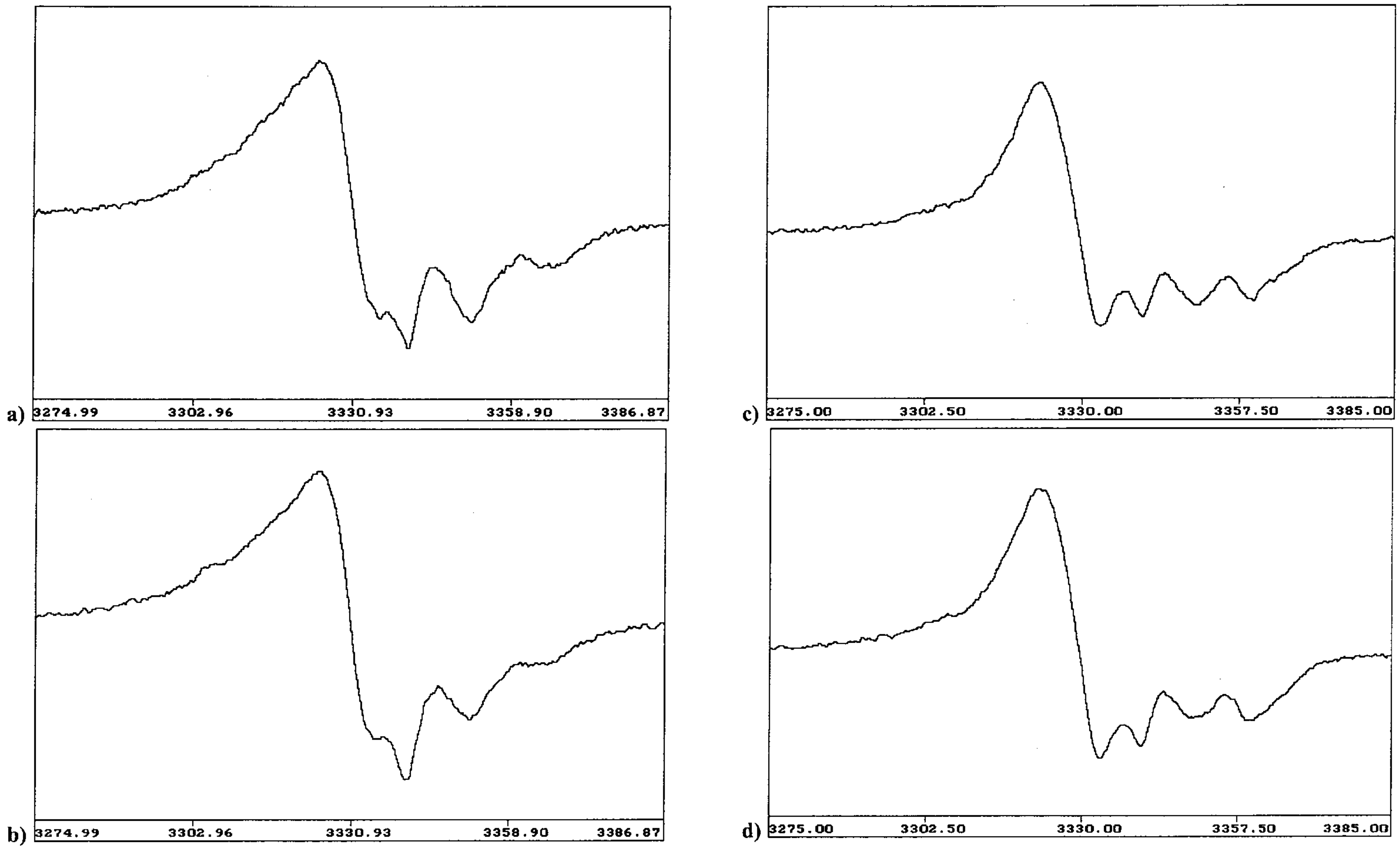


Fig. 4. ESR spectra of irradiated hexoses: a) D–galactose, b) L–galactose, c) D–mannose, d) L–mannose.

Table 1

Radiation-chemical yield (G) of hydrogen in irradiated hexoses.

Hexose	G_{H_2} (1/100eV)
D-Glucose	3,1 ± 0,2
L-Glucose	3,0 ± 1,0
D-Galactose	2,2 ± 0,3
L-Galactose	2,1 ± 0,6
D-Mannose	3,2 ± 0,9
L-Mannose	4,0 ± 0,5

ESR spectra of radicals formed in irradiated monosaccharides were similar. Samples of hexoses which were irradiated and investigated at 25°C gave poorly resolved signals (Figure 4) from secondary radicals mixture.

Formation of radicals in crystalline D–glucose, D–galactose (Figure 5) was similar to curves for irradiated ionic crystals. Rate of radicals disappearance in irradiated examples depended on temperature (Table 2). Radicals lived at 25°C for many months. Considerable acceleration of radicals destruction took place at the temperatures above 130°C (Figure 6).

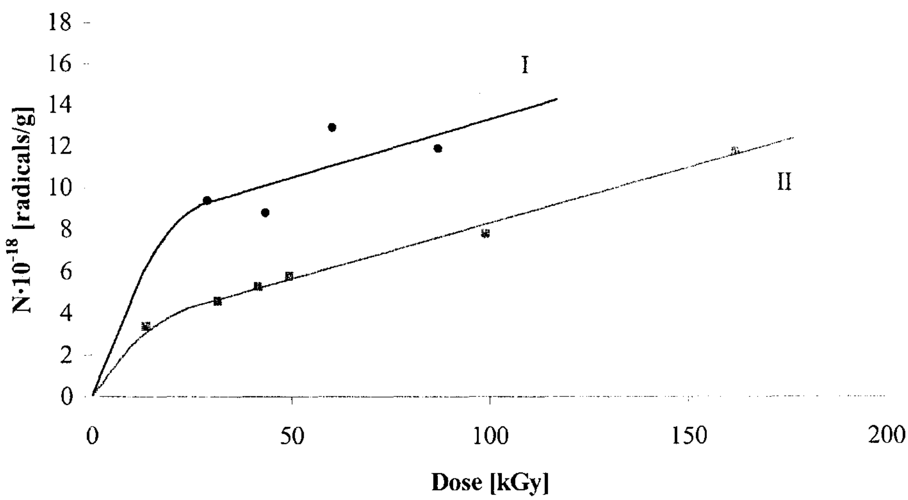


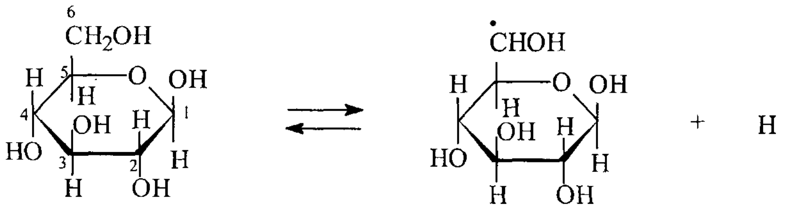
Fig. 5. Free radicals accumulation during γ-irradiation: I — D–glucose, II — L–glucose.

Table 2

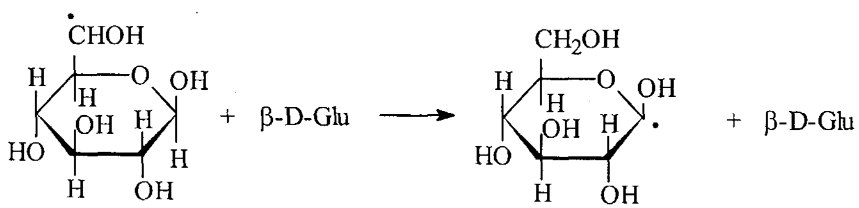
Dependence of relative quantity of living radicals on temperature after irradiation of D–galactose (dose 51.5 kGy, holding time 10 min).

T, °C	50	70	90	100	110	120	130
N/N_0	1.00	0.985	0.926	0.893	0.884	0.754	0.317

The nature of radicals in irradiated hexoses was not univocally determined [2, 5]. Based on [2] initial radicals which formed under irradiation, C_6 – primary hydroxyalkil radicals (I) could be observed. These radicals transformed at room temperature into secondary radicals (II) with unpaired electron at 1,2,3,4,5 C-atoms.



β-D-Glu (I) (2)



(I) (II) (3)

The radicals II might eliminate carbon monoxide and H_2O, producing small amounts of arabinose and 2-deoxyribose (G = 0.25) [2, 4].

There were two different portions on radicals accumulation curve (Figure 5). First of them characterized high G-value of radicals and finished at doses below 10 kGy. Accordingly, the integral G-values of radicals decreased with dose (Table 3).

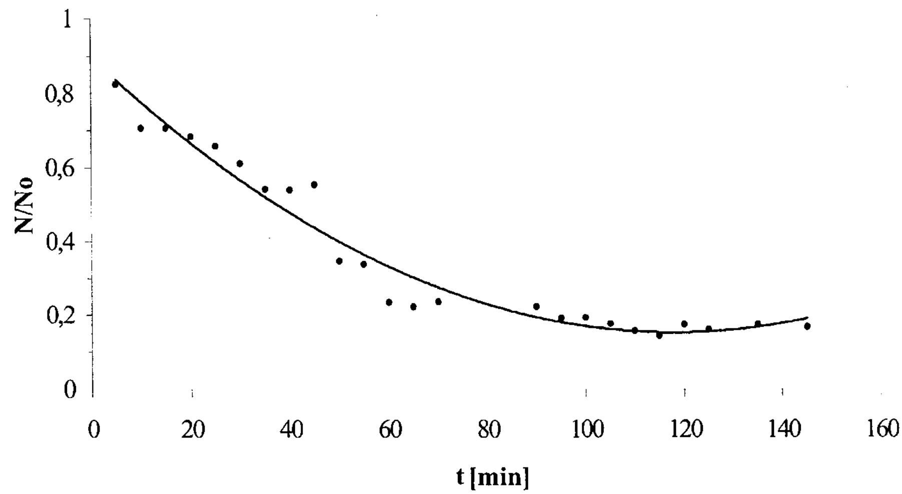


Fig. 6. Relative quantity of radicals vs. holding time of D–galactose.

Table 3

Radiation-chemical yield of radicals in irradiated saccharides.

Dose (kGy)	13,5	29	32	43	50	61	87	103	169
$G_{\alpha\text{-D-glucose}}$	–	5,2	–	3,3	–	3,4	2,2	–	–
$G_{\alpha\text{-D-galactose}}$	4,0	–	2,4	2,0	1,9	–	–	1,3	1,2

It was likely that, as in the case of ionic crystals, in the initial stage of radiolysis the inborn defects of crystal structure played an important role.

Process of radical disappearance at high temperature (Figure 6) could be described with a formal kinetics equation. However, strongly marked steps on curve suggested that radicals disappearance proceeded on polychronic kinetics law [6].

It was important to admit that alteration of OH-group location at C_2-atom did not change the G-value of radicals and H_2 (glucose and mannose). However, galactose was considerably more stable than glucose (Table 1 and 3). This fact rationalised an essential deposit of the C_4-H bond breaking process in formation of radical products and H_2.

Thus, radiation stability of D– and L–isomers of monosaccharides under action of non-polarised irradiation was identical. Radiation stability of galactose was one and a half times higher, than radiation stability of glucose and mannose. This fact proved a big role of a C_4-H bond breaking in process of radiolysis. Radicals, which form under irradiation of saccharides, left for several months, and it had to be taken into consideration on application of radiation-sterilized pills.

References

[1] McDonald T.: Acta Cryst., 1952, 654-659.
[2] Madden K., Bernhard W.: J. Phys. Chem., 1979, **83**, 2643–2649; 1982, **86**, 4033-4036.
[3] Bardsley J., Bauch P., Phillips G.: J. Chem. Soc., Perkin Trans., 1975, **2**, 614-618.
[4] Dizdaroglu M., Henneberg D., Neuwald K., Schomburg G., von Sonntag C.: Z. Naturforsch., 1977, **32b**, 213-224.
[5] Sharpaty V.: Rad. Biol. Ecol., 1999, **39**, 156-161.
[6] Bursztejn A., Klocichin W., Trachtenberg L.: Sov. J. Chem. Phys., 1984, **3**, 155-161.

WPŁYW PROMIENIOWANIA γ NA L- I D-MONOSACHARYDY

S t r e s z c z e n i e

Prześledzono wpływ promieniowania γ na D- i L-glukozę, D- i L-galaktozę oraz D- i L-mannozę w stanie polikrystalicznym. Głównym produktem gazowym radiolizy był wodór. Wydajność radiacyjna (G) wodoru zmieniała się od 2,2 (galaktoza) do 3,2 (1/100eV) (glukoza i mannoza). Widma ESR rodników powstające przez naświetlanie wszystkich heksoz były do siebie podobne i wskazywały na obecność mieszaniny wtórnych rodników. Scałkowana wartość G rodników obniżała się wraz z dawką promieniowania. Proces zaniku rodników można opisać równaniami kinetyki polichronicznej. Trwałość radiacyjna galaktozy była półtorakrotnie wyższa od radiacyjnej trwałości glukozy i mannozy. Usprawiedliwiało to istotny udział zrywania wiazań C_4-H w tworzeniu wodoru. Radiacyjna trwałość izomerów L- i D-monosacharydów przy zastosowaniu promieniowania niespolaryzowanego była identyczna.

Rodniki powstające z monosacharydów żyły w temperaturze pokojowej przez wiele miesięcy i fakt ten należy brać pod uwagę przy stosowaniu sterylizacji radiacyjnej.