2,6-Diamino-2,6-Didesoxy-D-Mannose und D-Rhamnosamin aus D-Glukosamin

N-Acetyl-D-glukosamin wurde in bekannter Weise[1]) zu N-Acetyl-D-Mannosamin-H_2O (I) epimisiert. I wurde mit Benzol/Äthanol azeotrop entwässert, mit auf gleiche Weise entwässertem Kationenaustauscher [Dowex-50(H^+-form)] versetzt und 15 Std langsam mit Äthanol/Benzol azeotrop destilliert. In 60% Ausbeute erhielten wir nach Abfiltrieren des Ionenaustauschers und Eindampfen der Lösung sirupöses Äthyl-N-Acetyl-D-mannosaminid (II).

Selektive 6-O-Tosylierung und nachfolgende Acetylierung lieferte in 35% Ausbeute Äthyl-N-acetyl-3,4-di-O-acetyl-6-O-tosyl-D-mannosaminid (III), Fp. 137—8°, $(\alpha)_D^{25} = +57°$ ($c = 2$, Pyridin). Die 6-Stellung der Tosylgruppe wurde bewiesen durch Reaktion mit Finkelsteins Reagenz[2]) zum 6-Jododerivat (IV), Fp. 56°, $(\alpha)_D^{25} = +47°$ (c = Pyridin), das nach Hydrierung an Raney-Nickel und nachfolgender Hydrolyse D-Rhamnosamin-HCl (V), Fp. 175° (Zers.), $(\alpha)_D^{25} = -19°$ ($c = 1$, H_2O), ergab. Das bereits synthetisierte L-Rhamnosamin-HCl[3]) zeigte Fp. 180° (Zers.), $(\alpha)_{Hg}^{22} = +26°$ ($c = 1.75$, H_2O).

III lieferte mit NaN_3 in Dimethylsulfoxid sirupöse, dünnschicht-chromatographisch reine 6-Azido-Verbindung, die an Pd in Methanol/Acetanhydrid zu Äthyl-2,6-diacetamido-2,6-didesoxy-3,4-di-O-acetyl-D-mannosid (VI), Fp. 227—8°, $(\alpha)_D^{25} = +74°$ ($c = 2$, Pyridin), hydriert wurde. Die Ausbeute von III bis VI betrug 70%. Hydrolyse von VI (2 N HCl, 4 Std Rückfluß) liefert in 65%iger Ausbeute 2,6-Diamino-2,6-didesoxy-D-mannose-2 HCl, Fp. 130—40° (aus Methanol/Isopropanol), $(\alpha)_D^{25} = +11°$ (10 min) $\rightarrow +4°$ (15 Std, Endwert) ($c = 2$, H_2O). Die Verbindung enthält Hydratwasser: $\frac{1}{2}$ H_2O nach 60 Std. Trocknen bei 56°, 3 Torr über P_2O_5.

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Influence of Ultraviolet Irradiation on Oscillopolarographic Behavior of Proteins

Some new data about the effects of UV light on a water solution of proteins are presented using the a. c. current oscillographic polarography[1–4]). The study was carried out using an electronic apparatus Polaroscope P 524 (Křižík, Prague) together with a dropping mercury electrode, which allowed us to follow the functions dE/dt against E. Solutions of horse serum albumin and globulin fractions, lysozyme, normal horse serum and egg white in the 0.2—2.0% concentrations were used for this study. Samples of proteins mentioned above were irradiated by UV light (2.537 Å) from a Philips TUV 30 W germicidal lamp. A part of solutions tested was left as a control withouth UV irradiation. Into the polarographic vessel containing always 1 ml of 1 N NaOH, the same volume of protein solution was added and immediately after mixing, oscillograms are taken. The main attention was drawn to a size of indentations which appeared on the oscillogram due to a change of capacity of the electrode double layer[4]) caused by adsorption and desorption of protein molecules in an interface of mercury drop electrode.

The depth of these indentations was distinctly reduced by UV irradiated proteins as compared with the corresponding native ones. Differences found in the oscillopolarographic behaviour of native and UV irradiated proteins mentioned above, depended on the dose of UV irradiation, on the concentration of irradiated protein solutions and on a kind of investigated protein finally.

In addition to a theoretical interest generally relating to the problems of protein denaturation, the present study provides a new rapid method for the detection of some photochemically, eventually also radiation-chemically induced lesions of protein molecules.

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Radioprotective Action of Calcium on Serratia marcescens

A radioprotective effect due to calcium has been observed in mice by administration of thyroid extract prior to irradiation[1]). In this connection a suggestion has been made that there is a relationship between the availability of calcium and cancer[2]). Now, further evidence to the "interaction" between calcium ion concentration and ionizing radiation has been shown with the gram negative soil bacterium Serratia marcescens. Suspensions of washed cells of Serratia marcescens (N.C.T.C. 1377) were prepared in sterile, glass distilled water. 10 ml. aliquots of this suspension were used for control and irradiation purposes. Calcium was added to a number of the aliquots so that they had a final concentration of 1.45×10^{-4} Ca^{2+}. Apart from exposures to ionizing radiation all samples were treated in an absoluty identical manner. Introduction of calcium ion to the suspension was found to have no effect on the viability of the organism in the absence of ionizing radiation. X-rays (230 kV; 15 mA) were used in these experiments and given at the rate of 534 rads per minute. After irradiation further dilutions were carried out and adjusted to give approximately the same number of organisms on each plate. Five plates were prepared from the dilutions of each control and irradiated suspension. The plates were incubated at 25° C for 48 hours. The statistical accuracy of counting each solution was the same as that found for normal samples.

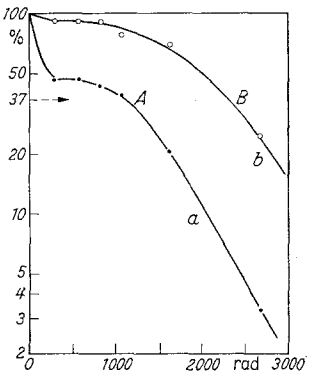

Fig. 1. Survival curve of Serratia marcescens without (curve *a*) and with (curve *b*: 1.45×10^{-4} M) calcium in suspension. Abscissa: dose (rad); ordinate: survival (%)

The results obtained from the irradiated suspensions with and without calcium ions present are shown in Fig. 1. The presence of calcium ions in the suspension had protected the organism. The dose-reduction factor for 37% survival of bacterial population was found to be 2.1. In Fig. 1 = (dose at point B)/(dose at point A).

The role of bivalent metal ions as the coupling factor between the rate of cell metabolism and rate of mutation is now better understood[3]). But it is not yet known how ionizing radiations interfere with the functions of bivalent metal ions. Certainly no evidence has been found that Ca^{2+} reacts directly with any of the radicals (.OH, .H, $e_{sol.}^-$) or molecular products (H_2, H_2O_2) resulting from the irradiation of water. Thus the radioprotective action of Ca^{2+} must lie in its ability to protect some part of the cell structure, and thus subsequently allow the continuation of normal biochemical processes. The membranes are the most likely structures in the cell which the calcium ions are protecting. The presence of these ions are known to stabilize the monolayers of fatty acids, proteins and lecithins; substances which are damaged directly or indirectly by ionizing radiations.

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Terpene aus dem Harz von *Araucaria imbricata*, Pavon *(A. araucana)*

Zur Untersuchung gelangte ein Harz, das in *Lonquimay* (Chile) gewonnen wurde und aus dem die wasserlöslichen Bestandteile durch Extraktion mit Wasser entfernt worden waren. Aus der ätherischen Lösung des Harzes ließen sich mit verd. Sodalösung größere Mengen saurer Bestandteile abtrennen, die, mit Mineralsäure in Freiheit gesetzt, eine sirupartige Flüssigkeit (I) lieferten. Die neutralen Anteile wurden mit Wasserdampf destilliert und ergaben geringe Mengen eines ätherischen Öles, in welchem gaschromatographisch neben Spuren verschiedener Sesquiterpene nur Limonen als Hauptbestandteil nachgewiesen wurde.

Nach Auskochen von I mit Petroläther hinterblieb ein in Petroläther unlöslicher Rückstand (II), der ausschließlich aus