MOLECULAR COMBINATIONS OF β-METHYL-*d*-GLUCOSIDE, β-METHYL-*d*-XYLOSIDE AND β-METHYL-*l*-FUCOSIDE WITH POTASSIUM ACETATE[1]

Sir:

While engaged in deacetylating tetraacetyl-β-methyl-*d*-glucoside with an alcoholic solution of potassium hydroxide, we observed the separation of a quantity of long silky needle-like crystals; these proved to represent a molecular combination of β-methyl-*d*-glucoside with potassium acetate ($C_7H_{14}O_6 \cdot CH_3COOK$). The same substance was prepared in quantity by mixing concentrated absolute alcohol solutions of the glycoside and of the anhydrous salt.[2] The α-methyl-*d*-glucoside when similarly treated in many experiments over a period of two years has never yielded any crystalline product. This specificity of the reaction constitutes its chief usefulness since it affords a convenient method of separating the beta form completely from its alpha isomer, a process which formerly was accomplished only by tedious fractionation. Application of this new double compound for such separations will be reported later.

The compound contains the sugar derivative and the salt in a molecular ratio of one to one as is indicated by the methoxyl and potassium analyses. It melts at 181–182° (corr.) and shows $[\alpha]^{20}_D$ in water $-22.0°$, which is the specific rotation that would be calculated on the assumption that the salt is inert and has no influence upon the rotation of the sugar derivative. The silky needles are rather hygroscopic.

The analogous compound of β-methyl-*l*-fucoside ($C_7H_{14}O_5 \cdot CH_3COOK$) is almost identical in superficial appearance, is similarly hygroscopic, melts at 208–212° (corr.) and shows $[\alpha]^{20}_D$ in water $+8.9°$. It is also a one to one molecular combination as indicated by its analyses and its specific rotation. This substance has been particularly valuable in facilitating the separation of β-methyl-*l*-fucoside from the alpha isomer, which forms no analogous compound, since the separation by fractionation was especially difficult in this case.

The β-methyl-*d*-xyloside potassium acetate compound ($C_6H_{12}O_5 \cdot CH_3COOK$), which is also of very similar appearance, is hygroscopic, melts at 171–172° (corr.), shows $[\alpha]^{20}_D$ in water $-41.3°$ and is likewise a one to one combination.

The glycoside may be recovered in each case by precipitating the potassium as potassium acid tartrate from a solution containing 50% of alcohol. By treating the double compounds directly with acetic anhydride, the acetylated methylglycosides may be obtained almost quantitatively, the salt acting as catalyst.

Efforts to prepare similar derivatives of α- and β-methyl-*d*-arabinoside, α- and β-methyl-*d*-galactoside, α- and β-methyl-*d*-lyxoside, α-methyl-*d*-xyloside, α-methyl-*d*-glucoside and α-methyl-*l*-fucoside have been unsuccessful. Other communications will follow.

NATIONAL INSTITUTE OF HEALTH
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RECEIVED AUGUST 27, 1934

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] The samples of commercial potassium acetate which we examined all contained a molecule of acetic acid of crystallization per molecule of salt, though the labels described the substance as CH_3COOK. The salt may be dried by heating at 150° but the same products are obtained from the methyl glycosides by using either the dried or the undried salt.

A NEW SYNTHESIS OF N-MONOPHENYLPIPERAZINE

Sir:

The only reported synthesis of N-monophenylpiperazine is that of V. Prelog and G. J. Driza [*Coll. Czechoslovak Chem. Comm.*, **5**, 497–502 (1933)].

The same synthesis had been accomplished by us in this Laboratory previous to the publication by the above authors. Since we had also noticed the physiological effects of N-monophenylpiperazine, it was decided to find, if possible, an easier and more convenient method for preparing it. This was desirable in view of the fact that we encountered considerable difficulty in preparing the intermediate bis-(β-haloethyl)-amines in sufficient quantities to make any large amounts of the N-monophenylpiperazine.

We have been able to prepare N-monophenylpiperazine in practically any amount by heating together aniline hydrochloride and diethanolamine hydrochloride at about 240° for from six to eight hours. In practice, the amines are mixed in molecular proportions and concd. hydrochloric acid added until the solution is neutral to litmus. The water is then boiled off and when the temperature has reached 220 to 240° it is kept there for from six to eight hours. Upon cooling the mass sets to a dark brown, gummy solid. The free base is liberated by treatment with concd. sodium hydroxide and the resulting oil is then fractionated in a vacuum, b. p. 156–157° (uncorr.) at 10 mm. (uncorr.). The yields are above 50% but vary considerably with the time of heating. Bis-(β-phenylaminoethyl)-amine is also formed but in smaller amounts.

N-Monophenylpiperazine is insoluble in water and soluble in all common organic solvents, d_4^{20} 1.0621; *neut. eq.* calcd. 162.1; found, 165.0. The hydrochloride of N-monophenylpiperazine was used for analysis for nitrogen. Calcd.: N, 14.11. Found: N, 14.01.

Other mono N-substituted amines have been prepared by this same method and their properties and derivatives will form the basis of a forthcoming publication.

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RECEIVED AUGUST 20, 1934

THE ISOLATION OF 0.1 GRAM OF THE OXIDE OF ELEMENT 91 (PROTACTINIUM)

Sir:

Using a process described previously [A. V. Grosse, *Ber.*, **61**, 233 (1928); THIS JOURNAL, **52**, 1742 (1930)] we have recently been able to work up large quantities of radium residues from Joachimsthal, Czechoslovakia. Thanks to the courtesy of the Lindsay Light Company, a small plant for the treatment of these residues was rigged up at their factory in West Chicago.

The technical process of concentration consists briefly: (1) an extraction of the residues, consisting principally of SiO_2, Fe_2O_3 and PbO with hydrochloric acid; (2) a melt of the silica residue, containing the protactinium, with sodium hydroxide, and (3) separation of the protactinium with zirconium phosphate from the mixture of basic oxides remaining after the melt is leached.

The starting material contains on the average 0.3 g. of protactinium per metric ton or a concentration of 1 part in 3 millions. The plant product contains the element in a concentration of 1 part in 5000, the yield being about 75%.

The plant product is further concentrated in the laboratory by a series of fractional crystallizations of zirconium oxychloride and zirconium phosphate precipitations. At a concentration of about 10% by weight of protactinium, most of the zirconium can be separated by sublimation of the chlorides; protactinium is then best precipitated directly by means of hydrogen peroxide. The purity of the oxide obtained by this method has been proved by x-ray analysis [H. Beuthe and A. V. Grosse, *Z. Physik*, **61**, 170 (1930)].

A detailed description of the technical and laboratory process will be given later.

Up to the present time, the plant product from about 1 ton of residues was worked up and 0.1 g. of protactinium oxide (Pa_2O_5) isolated in the pure state. Larger quantities will be isolated in the near future.

This work required by its very nature large financial expenditures and it has been made possible only by a generous grant of Mr. Hiram J. Halle of New York City, to whom we express our sincere gratitude. We are much indebted to Mr. A. C. Ratchesky, U. S. Minister to Czechoslovakia, and to Mr. Frank Novotny, U. S. Legation in Prague, for their efficient support in obtaining the raw material from the Czechoslovakian Government, and to Prof. Julius Stieglitz for his continuous help and advice.

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RECEIVED SEPTEMBER 10, 1934

METALLIC ELEMENT 91

Sir:

Isolation from radium residues of about 0.1 g. of protactinium oxide has been accomplished recently [A. V. Grosse and M. S. Agruss, THIS JOURNAL, **56**, 2200 (1934)]. The pure oxide (Pa_2O_5) was converted into the metal by two methods: (1) By bombarding the oxide, on a copper target, with a stream of electrons in a high vacuum. The use of 35,000-volt electrons for a few hours at a current strength of 5–10 milliamperes, splits the oxide into oxygen and the metal, the latter remaining as a shiny, partly sintered, metallic mass, stable in air. (2) By transforming it into a halide (Cl, Br, I) and then cracking it in a high vacuum (10^{-6} to 10^{-5} mm.) on an electrically heated tungsten filament, according to the reaction $2PaX_5 \longrightarrow 2Pa + 5X_2\uparrow$, the general method first introduced by Langmuir [I. Langmuir, THIS JOURNAL, **37**, 1139 (1915)]. The protactinium formed a shiny gray white, partly molten, deposit on the filament. The metal does not oxidize in air, in an expected contrast to metallic radium [Marie Curie and A. Debierne, *Compt. rend.*, **151**, 523 (1910)], and retains its luster for quite a while.