Bis-(5-nitro-2)-biphenylyl Diselenide (VII).—To a solution of 6 g. of potassium hydroxide in 30 ml. of methanol was added 2.8 g. of 2-selenocyano-5-nitrobiphenyl. The mixture was agitated and allowed to stand for one hour, then poured into a mixture of 200 ml. of benzene and 200 ml. of a saturated solution of aqueous boric acid. The yellow benzene layer was separated and the benzene evaporated. The product was recrystallized from acetone. There was obtained 1.9 g. (74%) of yellow crystals, m.p. 192–193°.

Anal. Calcd. for $C_{24}H_{16}N_2O_4Se$: Se, 28.4. Found: Se, 28.2

2-Nitrodibenzoselenophene (III).—To a solution of 1.5 ml. of bromine in 60 ml. of carbon tetrachloride was added 1.9 g. of the diselenide VII prepared above. The solution was warmed and then allowed to cool. Thirty ml. of acetone was added *cautiously* to remove excess bromine. The solution was refluxed for two hours. Then the solvents were evaporated, during which time hydrogen bromide was evolved. Thirty ml. of carbon tetrachloride was added to the residue and refluxing resumed for an additional two hours. The solvent was removed, during which time no hydrogen bromide fumes were evolved. The residue was extracted with two 200-ml. portions of hot methanol. The extractions were decolorized with Norit, and the volume reduced to about 100 ml. The cooled solution yielded 0.91 g. (49%) of yellow needles, m.p. 184–185°.

Anal. Calcd. for $C_{12}H_7NO_2Se$: Se, 28.5. Found: Se, 28.3.

Nitration of Dibenzoselenophene.—To a solution of 20 g. of dibenzoselenophene in 130 ml. of glacial acetic acid was added 8 ml. of fuming nitric acid. The solution was maintained at 65° until precipitation occurred. The mixture was cooled and filtered. The precipitate so obtained was recrystallized twice from benzene, yielding 11.5 g. (44%) of yellow needles, m.p. 184–185° (reported[1] 180°). This compound gave no depression in melting point when mixed with 2-nitrodibenzoselenophene prepared above.

The benzene filtrate was evaporated and the residue recrystallized three times from alcohol. Six grams (25%) of yellow solid, 4-nitrodibenzoselenophene, m.p. 133–134°, was obtained.

Anal. Calcd. for $C_{12}H_7NO_2Se$: Se, 28.5. Found: Se, 28.3.

2-Aminodibenzoselenophene.—Ten grams of Raney nickel in 150 ml. of benzene was placed in a Parr low-pressure hydrogenator for 15 minutes to reactivate the catalyst. To the container was added 6 g. of 2-nitrodibenzoselenophene, and the container was then reconnected to the hydrogenator. When the hydrogen pressure drop remained constant for 15 minutes, the charge was removed and filtered. Hydrogen chloride gas was passed through the colorless filtrate. The white precipitate formed was filtered and suspended in water, then an excess of ammonium hydroxide added. The precipitate was filtered and recrystallized from hexane, yielding 4.7 g. (86%) of colorless crystals, m.p. 92° (reported[2] 99°).

Deselenization.—To a hot solution of 1 g. of 2-nitrobenzoselenophene in 120 ml. of benzene was added 10 g. of Raney nickel. The mixture was heated on the Parr apparatus for 2 hours under 50 lb. pressure of hydrogen. The solution was then cooled and filtered. Hydrogen chloride gas was passed through the colorless filtrate, yielding 0.35 g. of a white precipitate (3-aminobiphenyl hydrochloride). Recrystallization of a portion of the hydrochloride from alcohol–ether brought the m.p. to 199–200°.

Anal. Calcd. for $C_{12}H_{12}NCl$: neut. equiv., 206. Found: neut. equiv., 212.

This amine was acetylated with acetic anhydride yielding 3-acetamidobiphenyl, m.p. 147° (reported[7] 148°). From the similar deselenization of 4-nitrodibenzoselenophene (II), was obtained a 63% yield of 3-aminobiphenyl hydrochloride. Mixtures of the hydrochlorides from deselenizations of the two nitro compounds showed no melting point depression. Mixtures of the two acetamidobiphenyls showed no melting point depression.

(7) F. Fichter and A. Sulzberger, *Ber.*, **37**, 882 (1904).

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COMMUNICATIONS TO THE EDITOR

IDENTIFICATION OF 3-KETOPENTOSE ARISING FROM RIBOSE PHOSPHATE

Sirs:

The formation of xylulose phosphate from ribose phosphate has been recently demonstrated in spleen extracts.[1] The present report is concerned with the isolation and tentative identification of *erythro*-3-ketopentose (*erythro*-3-pentulose) in the same system. Definitive identification must await synthesis of this compound.

Ribose 5-phosphate was incubated with a mouse spleen extract and the reaction product dephosphorylated and de-ionized as described previously.[1] The resulting free sugars were chromatographed on a Dowex-1–borate column. Xylulose and unreacted ribose were separated by elution with 0.02 *M* borate and ribulose by 0.04 *M* borate. The column was then eluted with 0.1 *M* borate and finally with 0.1 borate plus 0.25 *M* NaCl. Two small symmetrical peaks were located by means of reducing sugar assay.[2] These peaks were not observed when pure ribulose and xylulose were chromatographed under identical conditions.

The first of these peaks was lyophilized, freed from borate[3] and taken up in a small amount of water. The clear, slightly yellow solution contained approximately 17 μmoles determined as reducing sugar with either ribulose or arabinose as standard. Colorimetric analysis indicated that it was not glycolaldehyde, nor was it any recognizable triose, tetrose or hexose. The compound did give an orcinol and cysteine–carbazole reaction. In the latter case, a blue color was formed with a maximum at 600 mμ.[4] Paper electrophoresis in borate buffer yielded a single negatively charged spot.

The compound was subjected to periodic acid oxidation[5] as follows: 0.10 μ mole was incubated

(1) G. Ashwell and J. Hickman, THIS JOURNAL, **76**, 5889 (1954).

(2) J. T. Park and M. J. Johnson, *J. Biol. Chem.*, **181**, 149 (1949).

(3) L. P. Zill, J. X. Khym and G. M. Cheniae, THIS JOURNAL, **75**, 1339 (1953).

(4) A new and apparently specific colorimetric procedure has been devised whereby it is now possible to detect the compound in the original incubation mixture and to follow it throughout the isolation procedure.

(5) J. MacGee and M. Doudoroff, *J. Biol. Chem.*, **210**, 617 (1954).

with 0.25 ml. of 0.01 *M* sodium metaperiodate and 0.10 ml. 10 *N* H_2SO_4 for 20 minutes at 40°. Then 0.20 ml. of 0.10 *M* sodium arsenite was added and allowed to stand for 10 minutes at room temperature. The formaldehyde liberated was determined by the method of MacFadyen.[6] The compound yielded 1.81 moles of HCHO per mole of reducing sugar. When the unknown was reduced with KBH_4 before oxidation with HIO_4, the amount of HCHO liberated remained unchanged. A 3-ketopentose alone among the five carbon sugars possesses two terminal α-glycol groups and forms 2 moles of HCHO upon periodate oxidation. Prior reduction to the pentitol has no effect upon this ratio. This evidence must be regarded as presumptive rather than definitive since some 2-ketoses have been reported to form more than one mole of HCHO, although, according to Jackson,[7] the reaction producing 1 mole of HCHO predominates.

On reduction with borohydride, ribitol and xylitol were formed, as indicated by paper chromatography. To 1.5 μmoles of the unknown in 0.6 ml. of water, 0.20 ml. of a 0.01 *M* solution of KBH_4 was added and the mixture allowed to stand at room temperature for 20 minutes before adding 0.10 ml. of 2 *N* HCl to stop the reaction. The solution was de-ionized, lyophilized and taken up in 0.10 ml. of water. Upon paper electrophoresis in borate buffer, the unknown yielded three spots. As can be seen in Table I, a small amount of the unreduced compound remained at the end of the reaction while two new spots, corresponding to ribitol and xylitol, appeared. This result is unique for the 3-ketopentose with the *erythro* configuration since a *threo* 3-ketopentose would yield only one alcohol, arabitol.

TABLE I

The paper electrophoresis was performed at room temperature over a three-hour period. The potential remained constant at 500 volts while the amperage increased slightly from 10–12 ma. during the run. The solvent was 0.05 *M* borate buffer adjusted to *p*H 10. The spots were developed with the periodate spray of Metzenberg and Mitchell.[8]

Compound	Distance migrated from origin in cm.
Arabitol[a]	6.6
Ribitol[a]	7.4
Xylitol[a]	5.8
Unknown	9.1
Unknown after reduction	9.2, 7.4, 5.7

[a] The pure pentitols were generously provided by Dr. H. G. Fletcher of this Institute.

The second peak observed in the original fractionation procedure also produced a maximum at 600 mμ in the cysteine–carbazole reaction and appeared closely related to but not identical with the 3-ketopentose. As isolated from the column the solution had a faint blue color and contained copper in the ratio of 1 mole of copper to 2 moles of reducing sugar. The significance of this fraction is being further investigated.

Transketolase apparently plays no role in the conversion of ribulose phosphate to xylulose phosphate by spleen extracts,[1] as is also the case in certain bacterial preparations.[9] Therefore, we should like to suggest that the evidence presented above is consistent with the concept that the reaction proceeds through an ene-diol intermediate involving carbons 2 and 3 of ribulose. A tentative series of reactions may then be written which provides a mechanism for the formation of D-xylulose from D-ribulose and which also postulates the formation of 3-ketopentose. This formulation supports the view of Dische and Shigeura who proposed, on the basis of preliminary evidence, that the isomerization of ribose 5-phosphate leads to the formation of more than one carbonyl five carbon compound.[10] It should be further noted that a possible mechanism is hereby provided for the formation of L-xylulose from D-ribulose although, at the moment, experimental evidence for this is non-existent.

(6) D. A. MacFadyen, *J. Biol. Chem.*, **158**, 107 (1945).

(7) E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

(8) R. L. Metzenberg and H. K. Mitchell, THIS JOURNAL, **76**, 4187 (1954).

(9) P. K. Stumpf, unpublished data.

(10) Z. Dische and H. Shigeura, presented at the 126th meeting of the American Chemical Society, New York, N. Y., September, 1954.

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RECEIVED DECEMBER 22, 1954

RADIATION-INDUCED Ce(III)-Ce(IV) EXCHANGE IN AQUEOUS NITRIC AND SULFURIC ACIDS[1]

Sir:

The mechanism postulated by Allen[2] for the reduction of Ce(IV) in 0.4 *N* H_2SO_4 by radiation assumes a reaction of the form

$$Ce(III) + OH \longrightarrow Ce(IV) + OH^- \qquad (1)$$

as a vital step in the mechanism. Heretofore there has been no unequivocal experimental demonstration that any reaction involving the oxidation of Ce(III) actually does take place in irradiated cerium systems.

At the suggestion of Prof. Henry Taube[3] of the University of Chicago we have investigated the radiation-induced Ce(III)–Ce(IV) exchange in nitric and in sulfuric acid media.

Solutions containing unlabeled Ce(IV) and labeled Ce(III) were irradiated with unfiltered 50 kvp. X-rays from a tungsten target. After irradiation, the Ce(IV) was extracted with butyl phosphate[4] and the specific activity of this fraction determined. The radiation-induced exchange was calculated from this observed exchange rate by subtracting the spontaneous (thermal) exchange rate, which was determined by independent measurements.

The results are presented in Fig. 1 and Table I. We believe the exchange yields to be reliable to within 5–10% and the dosimetry yields to within 2%.

(1) This work was done under the auspices of the Atomic Energy Commission.

(2) A. O. Allen, *Radiation Research*, **1**, 85 (1954); Brookhaven National Laboratory Report BNL-1498.

(3) Consultant, Los Alamos Scientific Laboratory.

(4) J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).