

of other animals. Oxycellulose may prove useful as a fractionation medium for other purposes, where, for reasons of molecular structure or size, compounds are not amenable to separation with ion-exchange resins.

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RECEIVED MAY 7, 1951

SEDOHEPTULOSE IN PHOTOSYNTHESIS BY PLANTS¹

Sir:

Although its function has not been ascertained, the general occurrence of sedoheptulose,² D-altrioheptulose, in the succulent plants is well established. This sugar has not been identified in the majority of the members of the plant kingdom, but it now appears possible that its phosphate esters may perform a vital function during photosynthesis.

We have isolated labeled sedoheptulose monophosphate in C¹⁴O₂ photosynthesis products of all the plants thus far studied in this laboratory (*Chlorella*, *Scenedesmus*, *Rhodospirillum rubrum*, and the leaves of barley seedlings, soybean, alfalfa, sugar beet, spinach and geranium). It is invariably found as monophosphate esters. At least two such esters have been observed in radiograms of C¹⁴-labeled *Scenedesmus*. The major one is associated with fructose monophosphate while the minor one is inseparable, as yet, from glucose monophosphate. Sedoheptulose may be liberated enzymatically from its phosphates during the killing of the plant, but it has not been observed to accumulate in amounts exceeding the steady state concentrations of these phosphates. This suggests its participation only as a phosphate in most plants. These sedoheptulose phosphates are formed prior to hexose phosphates in the cases examined kinetically in this laboratory. In a typical experiment, one-second photosynthesis in C¹⁴O₂ by barley seedling leaves, the distribution of radioactivity among the neutral compounds obtained upon phosphatase hydrolysis of the mixed phosphates was as follows: 43% in fructose, 47% sedoheptulose and 7% in glucose.

Sedoheptulose, isolated chromatographically³ from phosphatase ("Polidase") hydrolysates of similarly separated phosphate esters,³ was identified by the following tests. (1) Two-dimensional paper co-chromatography with authentic sedoheptulose⁴ showed identical positions of the sugar and the radioactivity. The position of the authentic specimens was determined by resorcinol spray test. (2) The radioactive sugar in tracer concentrations is readily converted to sedoheptulosan by five-minute heating in 1 N hydrochloric acid. It was identified by co-chromatography with sedoheptulosan prepared similarly from an authentic specimen.

(1) This work was sponsored by the United States Atomic Energy Commission.

(2) F. B. LaForge and C. S. Hudson, *J. Biol. Chem.*, **30**, 61 (1917).

(3) A. A. Benson, J. A. Bassham, M. Calvin, T. Goodale, V. Haas and W. Stepka, *THIS JOURNAL*, **72**, 1710 (1950).

(4) A sample was kindly supplied by Mr. E. W. Putman of the Division of Plant Nutrition of this University.

(3) The equilibrium constant of the dehydration of the radioactive compound was found to be 4.0 as reported by LaForge and Hudson² for sedoheptulose. (4) Catalytic hydrogenation gave D-β-mannoheptitol, which was identified by co-chromatography with an authentic specimen prepared from sedoheptulose. (5) Periodate oxidation of both the hexose and the heptitol gave the expected amounts of products. The sedoheptulose obtained from five minutes C¹⁴O₂ photosynthesis by soy bean leaves gave 14.4% of formaldehyde activity, 28% glycolic acid activity and 55% of formate activity. The heptitol obtained from this compound had a formate/formaldehyde ratio of 3.1 compared to an expected 2.5 for uniform labeling.

The examination of the kinetics of formation of the phosphate esters involved in C¹⁴O₂ fixation⁵ and a detailed description of the identification will be published.

This early synthesis of sedoheptulose in CO₂ fixation and its stereochemical deviation from that of glucose strongly suggests its participation in a C₂ regenerative system for the primary CO₂-acceptor rather than as a hexose precursor. The predominant role of malic acid in "succulent metabolism" may well be related to the accumulation of sedoheptulose in these plants.

(5) A. A. Benson, S. Kawaguchi and M. Calvin, to be published.

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RECEIVED MAY 7, 1951

THE STRUCTURE OF JERVINE. II.¹ DEGRADATION TO PERHYDROBENZFLUORENE DERIVATIVES

Sir:

In a recent publication,¹ in which it was shown that the double bond conjugated with the inert keto group in jervine cannot occupy the 8,9-position as postulated by Jacobs and Sato,² we implied that this alkaloid does not have a normal steroid nucleus. We now present some of the evidence on which this assertion is based.

Jervine on treatment with acetic anhydride and zinc chloride at 140° yielded a dienone C₂₃H₃₀O₃, I (m.p. 186–188°, ³[α]²⁵_D –101°, ³λ^{alc.}_{max.} 300 mμ (4.4)³; calcd.: C, 78.02; H, 8.48; acetyl, 12.2; found: C, 78.14; H, 8.58; acetyl, 11.5), while isojervine¹ was merely acetylated under these conditions. I was cleaved by chromic acid into acetaldehyde and the yellow 1,4-diketone C₂₁H₂₆O₄, II (m.p. 181–183°; [α]²⁵_D –234°; λ^{alc.}_{max.} 267 mμ (4.16); 415 mμ (1.77); calcd.: C, 73.66; H, 7.62; acetyl, 12.6; found: C, 73.53; H, 7.87; acetyl, 13.5). Monoxime (m.p. 243–245°). Alkali readily converted II into the phenol III (diacetate, m.p. 207–209°; [α]²⁴_D –139°; calcd. for C₂₃H₂₆O₅: C, 72.23; H, 6.85; acetyl, 22.5; found: C, 72.58; H, 6.94; acetyl, 20.6), the ultraviolet charac-

(1) Paper I of this series: O. Wintersteiner, M. Moore, J. Fried and B. M. Iselin, *Proc. Nat. Acad. Science*, in press.

(2) W. A. Jacobs and Y. Sato (a) *J. Biol. Chem.*, **175**, 57 (1948); (b) **181**, 55 (1949).

(3) All melting points corrected; all rotations in chloroform; ultraviolet data: figures in parentheses denote log ε.