COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS AND PROPERTIES OF D-ERYTHROSE-4-PHOSPHATE

Sir:

D-Erythrose-4-phosphate has been postulated as an intermediate in carbohydrate metabolism, arising from sedoheptulose phosphate or fructose phosphate by the action of transaldolase[1] and transketolase,[2] respectively. However, the failure of this substance to accumulate in these systems, and the failure to trap it as a derivative, have prevented the direct demonstration of the involvement of this 4-carbon sugar in the reactions studied and, furthermore, have prevented a study of its properties.

We wish to report the synthesis of D-erythrose-4-phosphate by an unequivocal method similar to that used recently in the new synthesis of D-glyceraldehyde-3-phosphate.[3] D-Erythrose diethyl mercaptal, formed by the action of ethyl mercaptan and concentrated hydrochloric acid on 2,3-*O*-isopropylidene-D-erythrose[4] or D-erythrose prepared from D-arabinose by the disulfone degradation,[5] was converted to the crystalline 4-*O*-trityl-2,3-di-*O*-acetyl-D-erythrose diethyl mercaptal, m.p. 105–106°, $[\alpha]_D$ +3.7° (*c* 4, chloroform). Calculated for $C_{31}H_{35}O_5S_2$ (552.7): C, 67.4; H, 6.6; S, 11.6. Found: C, 67.2; H, 6.7; S, 11.5. The mercaptal was deacetylated and then demercaptalated in methanol to give the dimethyl acetal isolated as 4-*O*-trityl-2,3-di-*O*-benzyl-D-erythrose dimethyl acetal, m.p. 122–124°, $[\alpha]_D$ +18.3° (*c* 3, chloroform). Calculated for $C_{39}H_{36}O_7$ (616): C, 76.0; H, 5.8; OCH_3, 10.1. Found: C, 75.8; H, 5.9; OCH_3, 10.5. Following debenzoylation, this product consumed one mole of periodate per mole, as required if the trityl group occupied position 4. Reductive detritylation gave 2,3-di-*O*-benzoyl-D-erythrose dimethyl acetal (not isolated), which was phosphorylated to 4-diphenylphosphoryl-2,3-di-*O*-benzoyl-D-erythrose dimethyl acetal. This substance was unblocked by reductive cleavage of the phenyl groups with hydrogen and platinum, followed by saponification of the ester groups to give 4-phosphoryl-D-erythrose dimethyl acetal, isolated as the crystalline cyclohexylammonium salt, m.p. 160–165°, $[\alpha]^{25}_D$ 0° ± 0.2° (*c* 5, water or 1 *N* hydrochloric acid). Calculated for $C_6H_{15}O_8P \cdot 1.5C_6H_{11}NH_2$ (395): C, 45.5; H, 8.7; N, 5.3; P, 7.9; OCH_3, 15.7. Found C, 45.4; H, 8.7; N, 5.6; P, 8.0; OCH_3, 16.1.

This compound consumed one mole of periodate per mole, consistent with the presence of two adjacent free hydroxyl groups. The acetal structure was readily hydrolyzed in aqueous solution at the *p*H of its own free acid (24 hours at 40°) to give D-erythrose-4-phosphate. The latter had no detectable rotation in acid or neutral solution. It is strongly reducing and gave the theoretical value by the Willstätter-Schudel alkaline iodine titration. The compound was decomposed in 1 *N* acid at 100°, and in 1 *N* alkali at room temperature with the elimination of inorganic phosphate at a rate similar to that for D-glyceraldehyde-3-phosphate.

This synthetic D-erythrose-4-phosphate couples readily with dihydroxyacetone phosphate in the presence of rabbit muscle aldolase to give a sedoheptulose phosphate ester that has the properties of the diphosphate described recently.[6] Enzymatic dephosphorylation yields sedoheptulose (characterized chromatographically), while acid hydrolysis results in the elimination of two moles of phosphate per mole at two distinctly different rates, comparable to the hydrolysis curve of fructose-1,6-diphosphate.

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THE PERTECHNETATE ION AS AN INHIBITOR OF CORROSION[1]

Sir:

In a theoretical study of alternative mechanisms to account for the action of corrosion inhibitors of the type of the chromate ion it was concluded that the property responsible for inhibition must involve the internal polarity of the XO_4^{n-} particle. This hypothesis led to the prediction that, of all the elements in groups V to VIII of the periodic system, technetium, in the form of the pertechnetate ion, TcO_4^-, was most likely to possess the requisite properties. This expectation has been amply confirmed. For example, it has been found that mild carbon steels may be effectively protected by from 5 to 50 p.p.m. of technetium element (5×10^{-5} to 5×10^{-4} *f* $KTcO_4$) in aerated distilled water at temperatures up to at least 250°. Certain specimens have been observed at room temperature for over two years with no evidence whatever of attack.

The favorable nuclear and chemical properties of technetium have made it possible to investigate several questions bearing upon the mechanism of the inhibitory process. Thus, it has been found possible to achieve inhibition under very corrosive conditions without depositing more than 3×10^{12} atoms of technetium per sq. cm. It also was shown that the inhibition depends upon the maintenance of some minimum concentration of inhibitor, though there appears to be no continuous reduction of it over long periods of time.

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