bered ring. The facts that in III the tertiary hydroxyl and the methoxyl cannot be beta to the secondary hydroxyl, and that IX does not react with periodate, severely limit the possible arrangements of the three oxygen functions on the ring in III. The conversion of IX to perhydrobenzofuran derivatives, the structure of one of which is established by synthesis,[17] indicates the correctness of structures IX, III and II.

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[17] D. D. Chapman, *et al.*, THIS JOURNAL, **82**, 1009 (1960).

[18] Abbott Laboratories Fellow, 1957–1958.

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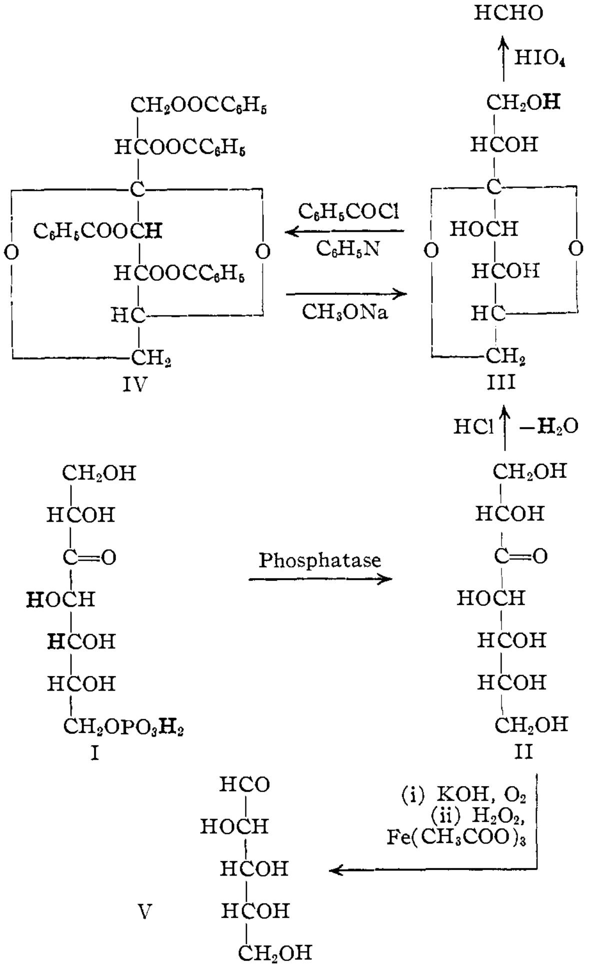
3-KETO-D-ARABOHEPTOSE PHOSPHATE: PROPOSED STRUCTURE FOR A NEW HEPTULOSE PHOSPHATE[1]

Sir:

In a previous communication,[2] we reported the isolation of a new heptulose phosphate from a digest of rat liver supernatant plus glucose 6-phosphate (G6P) as well as some properties of the heptulose, its phosphate, anhydride and anhydride tetrabenzoate. Evidence supporting its structure as 3-keto-D-*arabo*heptose phosphate (I) is now presented.

Phosphatase ("polidase") hydrolysis of I (free of other sugar phosphates) yielded the free sugar II which exhibits positive color reactions for ketose (resorcinol HCl; naphthoresorcinol-HCl and α-naphthylamine phosphoric acid) and for ketoheptose by the orcinol trichloroacetic acid reagent. II was degraded first by alkali oxidation[3] and then by ferric acetate–H_2O_2[4] to a pentose V. This was identified as arabinose by circular paper chromatography in two separate solvent systems[5] and by its crystalline diphenylhydrazone (2 mg.) m.p. 202.5°. The mixed melting point with authentic D-arabinose diphenylhydrazone (m.p. 202.5°) was not depressed. Acid treatment[6] of II yielded an anhydride III which was converted to the pure crystalline tetrabenzoate derivative[2] IV. Debenzoylation of IV (3 mg.) with sodium methoxide reagent produced III, which was oxidized with periodate to yield an equimolar amount of formaldehyde.[7] Gluco- and mannoheptulose[8] exhibited a rate of migration on paper different from II in butanol–pyridine–water (6:4:3).



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[2] H.-G. Sie, V. N. Nigam and W. H. Fishman, THIS JOURNAL, **81**, 6083 (1959).

[3] N. K. Richtmyer, R. M. Mann and C. S. Hudson, *ibid.*, **61**, 343 (1939).

[4] H. G. Fletcher, Jr., H. D. Diehl and C. S. Hudson, *ibid.*, **72**, 4246 (1950).

[5] Acetone:butanol:water (7:2:1) and butanol:pyridine:water (6:4:3) separate ribose and arabinose completely in six hours. The pentose consistently occupied the arabinose position. The conditions of degradation were ones which yield ribose only from sedoheptulose[8] and this fact was confirmed in this laboratory with both solvent systems.

[6] H.-G. Sie, V. N. Nigam and W. H. Fishman, *J. Biol. Chem.*, **234**, 1955 (1959).

[7] D. A. McFadyen, *ibid.*, **158**, 107 (1945).

[8] We thank Dr. H. S. Isbell, National Bureau of Standards, Washington, D. C., for making these reference sugars available to us.

NOVEL THERMAL REARRANGEMENTS ACCOMPANYING ACETATE PYROLYSIS IN SMALL RING SYSTEMS

Sir:

Pursuant to the preparation and the polymerization of vinylcycloalkanes, the acetate pyrolysis procedure[1,2] was applied to esters of secondary alcohols bearing an alpha carbocyclic group. We wish to report the discovery that the principal product from the pyrolysis of 1-cyclopropylethyl acetate was *cyclopentene* and that from 1-cyclobutylethyl acetate was *cyclohexene*. The pyrolysis of 1-cyclopentylethyl acetate proceeded in the reported manner[3] while the pyrolysis of 3-cyclohexenylmethyl acetate yielded 4-methylenecyclohexene, 60%, toluene, 24%, and methylenecyclohexene, 3%.

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[1] C. G. Overberger and D. Tanner, THIS JOURNAL, **77**, 369 (1955).

[2] W. J. Bailey and W. F. Hale, *ibid.*, 647 (1959), and previous references.

[3] J. R. van der Bij and E. C. Kooijman, *Rec. trav. chim.*, **71**, 837 (1952).