

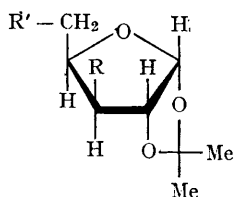
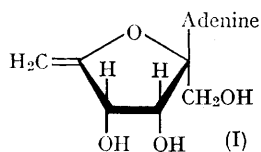
Furanoid Vinyl Ethers

By L. HOUGH and B. OTTER

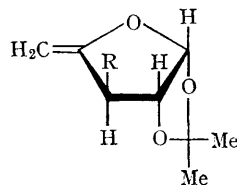
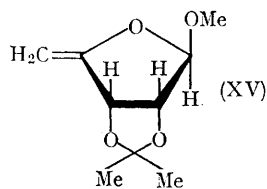
(The School of Chemistry, The University, Bristol)

ELIMINATION of hydrogen halide from 6-halogeno-D-glucopyranoid derivatives was first observed by Helferich and Himmen.¹ This Communication reports the extension of this reaction to the pentofuranoid and hexulofuranoid series to give exocyclic vinyl ethers which are of interest in view of the revised structure of the antibiotic angustmycin A²

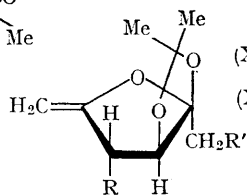
Treatment of 3-O-acetyl-5-deoxy-5-iodo-1,2-O-isopropylidene- α -D-xylofuranose (IV) with anhydrous silver fluoride in pyridine afforded an 83% yield of a crystalline unsaturated sugar, m.p. 31–33°, which was shown to be 3-O-acetyl-5-deoxy-1,2-O-isopropylidene- β -L-threo-pent-4-enofuranose (VI). Because the asymmetry at C-4 is destroyed



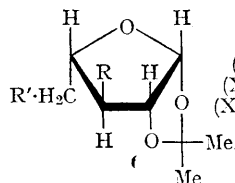
- (II) R = OH; R' = O·SO₂·C₆H₄·Me
 (III) R = OH; R' = I
 (IV) R = O·CO·Me; R' = I
 (V) R = R' = O·SO₂·C₆H₄·Me.



- (VI) R = O·CO·Me
 (VII) R = OH
 (VIII) R = O·CO·Ph
 (IX) R = O·SO₂·C₆H₄·Me



- (XIII) R = O·CO·Me;
 R' = O·CO·Ph
 (XIV) R = R' = OH



- (X) R = OH; R' = I
 (XI) R = O·CO·Me; R' = I
 (XII) R = R' = O·SO₂·C₆H₄·Me

(decoyinine) (I) and the growing attention to unsaturated carbohydrates.³

in this reaction, it was possible to prepare this vinyl ether (VI) from the L-arabino-isomer (XI).

Catalytic deacetylation of (VI) with sodium methoxide in methanol afforded a quantitative yield of syrupy 5-deoxy-1,2-*O*-isopropylidene- β -*L*-threo-pent-4-enofuranose (VII), which was further characterized as the crystalline 3-*O*-benzoate (VIII), m.p. 52—54°. 5-Deoxy-5-iodo-1,2-*O*-isopropylidene- α -*D*-xylofuranose⁴ (III) failed to yield an unsaturated compound when treated with silver fluoride but instead there was isolated in 85% yield the oxetan, 3,5-anhydro-1,2-*O*-isopropylidene- α -*D*-xylofuranose. This compound, first prepared by Levene and Raymond⁵ by reaction of the 5-*O*-tosylate⁴ (II) with sodium methoxide, also resulted from the interaction of (II) with silver fluoride. However, 5-deoxy-5-iodo-1,2-*O*-isopropylidene- β -*L*-arabinofuranose⁶ (X), where the stereochemistry prohibits anhydro-ring formation, reacted with silver fluoride to give the vinyl ether (VII) which was best isolated as the 3-*O*-acetate (VI). Both 1,2-*O*-isopropylidene-3,5-di-*O*-tosyl- α -*D*-xylofuranose⁷ (V), and the corresponding *L*-arabino-isomer⁸

(XII) underwent an elimination reaction induced by silver fluoride. The reaction was slow, however, and the product, 5-deoxy-1,2-*O*-isopropylidene-3-*O*-tosyl- β -*L*-threo-pent-4-enofuranose (IX), was best prepared by esterification of the vinyl ether (VII) with toluene-*p*-sulphonyl chloride.

Good yields of the syrupy vinyl ethers (XIII) and (XV) were obtained from 4-*O*-acetyl-1-*O*-benzoyl-6-deoxy-6-iodo-2,3-*O*-isopropylidene- α -*L*-xylo-hexulofuranose and methyl 5-deoxy-5-iodo-2,3-*O*-isopropylidene- β -*D*-ribofuranoside⁹ respectively. Catalytic de-esterification of (XIII) afforded the crystalline 6-deoxy-2,3-*O*-isopropylidene- β -*D*-threo-hexulo-5-enofuranose (XIV).

The chemistry of the foregoing vinyl ethers, all of which had elemental analyses and spectral characteristics consistent with the structures assigned, is currently under investigation in this laboratory.

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³ R. J. Ferrier, *Adv. Carbohydrate Chem.*, 1965, **20**, 67.

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⁷ P. Karrer and A. Boettcher, *Helv. Chim. Acta*, 1953, **36**, 837.

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⁹ P. A. Levene and E. T. Stiller, *J. Biol. Chem.*, 1934, **104**, 299.