The Synthesis of Coriose

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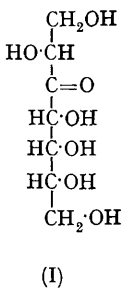
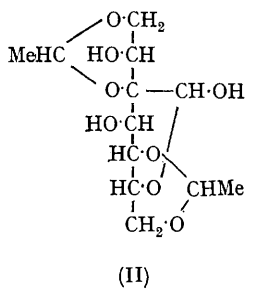
CORIOSE, the first naturally occurring 3-ketose, to which the structure D-*altro*-3-heptulose (I) was assigned,[1] has now been synthesized *via* aldol condensation of 2,4-*O*-ethylidene-D-erythrose.[2]

Crystalline 1,3 : 5,7-di-*O*-ethylidene-3-*C*,6-*O*-hydroxymethylene-D-*glycero*-D-*talo*-heptitol (II)[3] was removed from the syrupy mixed product of the aldol condensation. D-*manno*-3-Heptulose (III), which is the first synthetic 3-heptulose, had been obtained from (II) by Schaffer.[3] The mother-liquors of the aldol condensation may contain (II) and possibly its three C-3 and C-4 stereoisomers. Two of them, (IV) and its C-3 epimer, should yield (I) on hydrolysis followed by lead tetra-acetate oxidation, upon which preferential cleavage[4] is expected to occur between C-3 and the potential formyl group attached to it.

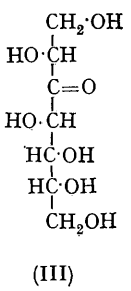
The mother-liquors of (II) were hydrolysed and then oxidized with about 1 mole equivalent of lead tetra-acetate. After removal of aldoses by bromine oxidation followed by treatment with ion-exchange resins, the syrupy product showed on paper-partition chromatography (n-butanol–pyridine–water, 6 : 4 : 3; colouring reagent: orcinol–trichloroacetic acid) two dark brown spots corresponding to (I) (R_F 0·40) and (III) (R_F 0·35). Identification was effected by g.l.c. of the trimethylsilyl ether. This crude product was purified by preparative paper chromatography (n-butanol–ethanol–water, 4 : 1 : 1·2). The methanolic extract from the area of 3-heptuloses yielded a crystalline product upon seeding with (I), and this product was identified by i.r. spectra and mixed m.p. with coriose isolated from *Coriaria japonica* A. Gray.



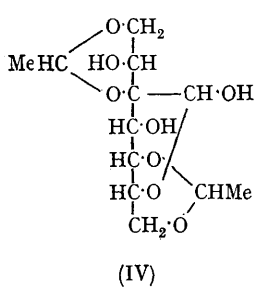
(I)



(II)



(III)



(IV)

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[1] T. Okuda and K. Konishi, *Chem. Comm.*, 1968, 553.

[2] The isomerisation of sedoheptulose in boiling pyridine to D-*altro*-3-heptulose and the identification of the latter with one of the products from *Primula officinalis* Jacq. was reported by R. Begbie and N. K. Richtmeyer, *Carbohydrate Res.*, 1966, **2**, 272.

[3] R. Schaffer, *J. Amer. Chem. Soc.*, 1959, **81**, 2838; *J. Org. Chem.*, 1964, **29**, 1473.

[4] A. S. Perlin and C. Brice, *Canad. J. Chem.*, 1956, **34**, 85, 514.