Isolation and Structure of Coriose, a Natural 3-Heptulose

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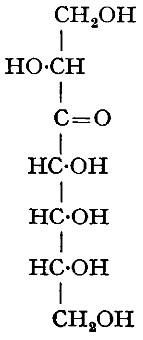
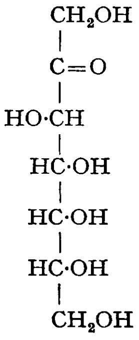
A NOVEL type of natural heptulose (I) has been isolated from the fruit and the extract of leaf and stem of *Coriaria japonica* A. GRAY. The isolation was carried out by treating the mother liquor of the extraction of tutin[1] and coriamyrtin[2] with yeast, and passing the resultant liquor through ion-exchange resins and a charcoal–Celite column. Besides this natural heptulose, sedoheptulose (II), *myo*-inositol, and methyl α-D-galactoside were isolated from the red fruit. Sedoheptulose and *myo*-inositol were isolated from the extract of leaf and stem, and volemitol (III) from the seed.

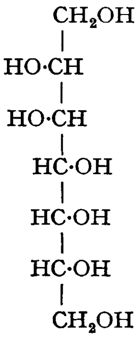
This reducing sugar (I), m.p. 169—171°, $[\alpha]_D^{27}$ + 21·7° (equilibrium in water), behaved as a ketose on the hypoiodite oxidation, and yielded a tarry product on the reaction with phenylhydrazine under the analogous reaction condition as the formation of glucosazone. These properties are identical with those of the sugar which was isolated from the stem of the same plant by Kariyone *et al.*,[3] who named it coriose and regarded it as a new hexulose.

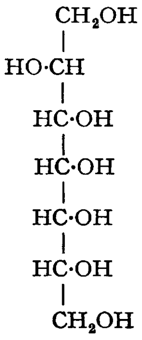
Coriose was recovered from the treatment with hot dilute N-hydrochloric acid for 1 hr., and moved on the paper chromatogram (p.p.c.) as fast as glucose (R_F 0·18 in n-butanol–acetic acid–water, 4 : 1 : 5), or faster than glucose (R_F 0·40 in n-butanol–pyridine–water, 6:4:3). A crystalline benzoate, m.p. 100—102°, was produced, whose analysis and n.m.r. spectrum are indicative of the molecular formula, $C_{42}H_{34}O_{12}$, which corresponds to a heptose-pentabenzoate.

The sodium borohydride reduction of (I) yielded a mixture from which polyalcohols, m.p. 153—154°, and m.p. 125—128°, were isolated and identified with synthetic volemitol (III)[4] and D-*glycero*-D-*altro*-heptitol (IV)[5] respectively. Upon the oxidation of (I) in cold 1N-KOH with oxygen at 0—2°, in a similar way as the oxidative degradation of (II) *etc.*,[6] 1 mole of oxygen was consumed within 2 days. After treating with resin, the ether extract showed a spot of glycolic acid on p.p.c. and thin-layer chromatogram, and the mother liquor showed a spot corresponding to a pentanolactone on p.p.c. The latter product was reduced with sodium amalgam to a pentose which was identified with ribose on p.p.c. with three kinds of solvent mixture and g.l.c. of the trimethylsilyl ether.


(I)


(II)


(III)


(IV)

These results indicate that the structure of coriose is D-*altro*-3-heptulose (I), which is the first instance of a 3-ketose occurring in nature. Further supports of this structure were provided as follows: the solution of (I) in lime water at room temperature showed on p.p.c. that Lobry de Bruyn-Alberda van Ekenstein rearrangement[7] slowly took place. Acid treatment of the product yielded a crystalline anhydride which was identified as sedoheptulosan[8] to prove that (II) was produced by the rearrangement. Faster rearrangement was observed in 1N-KOH at room temperature. However, (I) was recovered mostly unchanged from a solution in cold 1N-KOH which was kept at 0° for 24 hr. to prove that the oxidative cleavage of (I) in cold 1N-KOH mostly proceeded without being accompanied by the rearrangement. Upon the oxidation of (I) with 2 mole equivalent of lead tetra-acetate, according to the method of Perlin and Brice[9] which should cause the preferential cleavage at C(3)–C(4) in the hemiketal ring, D-glyceraldehyde and D-glyceric acid were produced.

The presence of this unique sugar in the plant was confirmed by p.p.c. of the juices pressed from fresh fruit and stem, and also by the g.l.c. after treating the juice with yeast. Methyl α-D-galactoside was also identified by g.l.c.

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