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# DERIVATIVES OF 5-DEOXY-5-MERCAPTO-D-GLUCOSE[1]

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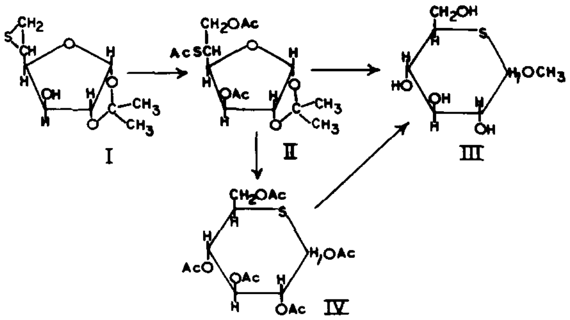
IN the course of syntheses of sugars wherein the ring oxygen atom is replaced with another hetero atom,[2] the sulfur containing analog of D-glucose has been prepared.



The known 5,6-episulfide analog of 1,2-O-isopropylidene-α-D-glucofuranose (I)[3] is acetolyzed with a solution composed of potassium acetate, acetic acid and acetic anhydride (1:2:10 w/v) at 140° for 4 hr. These conditions are similar[4] to those used to open the 5,6-episulfide ring in the L-idose analog. It is then poured into ice-water to produce crystalline

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[1] Journal Paper No. 1925 of the Purdue University Agricultural Experiment Station, Lafayette, Indiana.

[2] R.L. Whistler, M.S. Feather and D.L. Ingles, J. Amer. Chem. Soc. 84, 122 (1962).

[3] L.D. Hall, L. Hough and R.A. Pritchard, J. Chem. Soc. 1537 (1961).

[4] T.J. Adley and L.N. Owen, Proc. Chem. Soc. 418 (1961).

3,6-di-O-acetyl-1,2-O-isopropylidene-5-deoxy-5-thioacetyl-α-D-glucofuranose (II), m.p. 149°, $[\alpha]_D^{25}$ + 7.2° (c, 1.8 in chloroform). (Found: C, 49.68; H, 5.90; S, 9.18. Calc. for $C_{15}H_{22}O_8S$: C, 49.71; H, 6.12; S, 8.85). It is assumed that acetate ion attacks the episulfide ring in the same manner as it does the 5,6-anhydro compound thus giving rise to a D-gluco configuration[5] with sulfur attached to carbon 5. This material has the characteristic absorption[6] for thiol acetate at 230-240 mμ.

Acetolysis[7] of (II) with acetic anhydride, acetic acid, and sulfuric acid at 25° for 72 hr produces a chromatographically pure sirupy penta-acetate (IV), $[\alpha]_D^{25}$ + 41.3° (c, 2.9 in chloroform). (Found: Acetyl, 52.66; S, 8.04. Calc. for $C_{16}H_{21}O_{10}S$: Acetyl, 52.91; S, 7.89). This material shows no ultraviolet absorption corresponding to thiol acetate thereby confirming the presence of sulfur as the ring hetero atom.

Paper chromatograms indicate that acid hydrolysis of either (II) or (IV) produces complex mixtures of materials.

Methanolysis of (II) with 5 per cent methanolic hydrogen chloride at 37° to constant optical rotation (24 hr) produces sirupy methyl D-glucothiapyranoside (III). Methanolysis of (IV) likewise produces the same glycoside, which after chromatographic purification has $[\alpha]_D^{25}$ + 208.0° (c, 0.9 in methanol). (Found: S, 14.90; $OCH_3$, 14.77. Calc. for $C_7H_{14}O_5S$: S, 15.26; $OCH_3$, 14.77). This material showed no thiol activity when titrated with iodine in acetic acid solution.[8]

The glycoside consumes 4 moles of periodate, part probably going to the oxidation of the sulfur atom,[9] and it produces 1.8 moles of titratable acid. Formic acid, estimated by titration of steam distillates of the oxidation solution, is present to the extent of 1 mole/mole of glycoside thus confirming the presence of a pyranose ring.

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[5] H. Ohle and W. Mertens, Ber. Dtsch. Chem. Ges. 62B, 2176 (1935); S. Peat, Advanc. Carbohydrate Chem. 2, 37 (1946).

[6] H.P. Koch, J. Chem. Soc. 387 (1949).

[7] A.T. Ness, R.M. Hann and C.S. Hudson, J. Amer. Chem. Soc. 66, 665 (1944).

[8] R.M. Evans and L.N. Owen, J. Chem. Soc. 224 (1949).

[9] N.J. Leonard and C.R. Johnson, J. Org. Chem. 27, 282 (1962).