Isopropylidene Acetals of 5-Thio-D-ribose and 5-Thio-D-xylose

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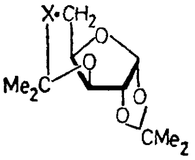
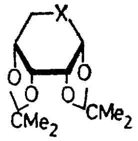
Summary Both 5-thio-D-ribose and 5-thio-D-xylose react with acetone and 2,2-dimethoxypropane respectively to give 1,2:3,4-di-*O*-isopropylidene-α-D-ribo- and xylo-pyranoses, no furanoid products were detected.

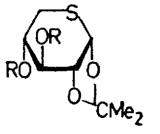
REDUCING carbohydrates having both hydroxyl and thiol groups suitably positioned for internal acetal formation show a preference for the incorporation of sulphur rather than oxygen in the sugar ring.[1] This preference is also shown in their esters,[1] glycosides[1] and thioglycosides.[2] We now report the first examples of isopropylidene acetals which follow this trend.



(1) X = O
(4) X = S



(2) X = O
(5) X = S



(3) R,R = CMe$_2$
(6) R = H

Both D-ribose and D-xylose react with acidified acetone to give acetals of the furanose forms. Thus D-xylose gives the 1,2:3,5-diacetal (**1**)[3] and D-ribose gives both 1,2- and 2,3-acetals, mainly the latter, though a small amount of 1,2:3,4-di-*O*-isopropylidene-α-D-ribopyranose (**2**) is also obtained.[4]

5-Thio-D-xylose failed to react with acidified acetone but more forcing conditions, employing 2,2-dimethoxypropane in *NN*-dimethylformamide containing *p*-toluene sulphonic acid, gave 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-xylopyranose (**3**). The structure was demonstrated by the ^{1}H n.m.r. spectrum which was in agreement with an α-D-xylopyranoid system in the $^4C_1$ conformation. The compound was clearly distinguished from the isomer obtained[5] by the action of acidified acetone on 1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose whose ^{1}H n.m.r. spectrum clearly showed it to be 1,2-*O*-3,5-*O*,*S*-diisopropylidene-5-thio-α-D-xylofuranose (**4**).

By contrast 5-thio-D-ribose reacted with acidified acetone to give crystalline 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-ribopyranose (**5**) whose ^{1}H n.m.r. spectrum showed coupling constants very similar to those of the oxygen analogue (**2**) and suggestive of the $^3S_5$ conformation.

Both of these 1,2:3,4-pyranose diacetals are more strained, one containing a *trans*-acetal group and the other having a skew conformation, than possible furanose products, and their formation is further evidence of the strong preference of these thio-sugars to adopt the cyclic form having sulphur in the ring.

Mild acid hydrolysis of the xylodiacetal (**3**) yielded a crystalline monoacetal whose lack of reducing and thiol properties indicated it to be 1,2-*O*-isopropylidene-5-thio-α-D-xylopyranose (**6**). It gave a dibenzoate and a dimesylate.[6] Selective hydrolysis of the ribodiacetal (**5**) could not be achieved, in contrast to previous experience with the oxygen analogue (**2**).[4] It is known[7] that the glycosides of these thio-sugars are more easily hydrolysed than the related oxygen glycosides and it seems that this is also the case for the 1,2-acetals. The successful selective hydrolysis of the xylodiacetal (**3**) is presumably due to the greater lability of the 3,4-*trans*-acetal group.

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