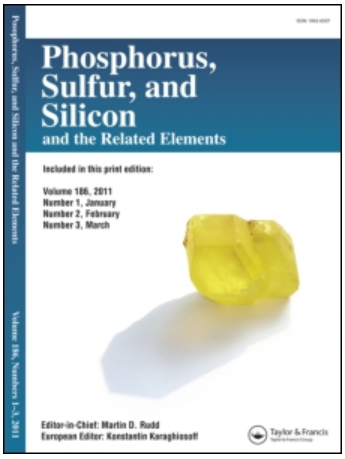

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Preparation and Reactions of 2-Oxa-6-thiabicyclo[3.2.0]-heptanes and 2-Oxa-5-thiabicyclo[2.2.1]heptanes from Pentoses

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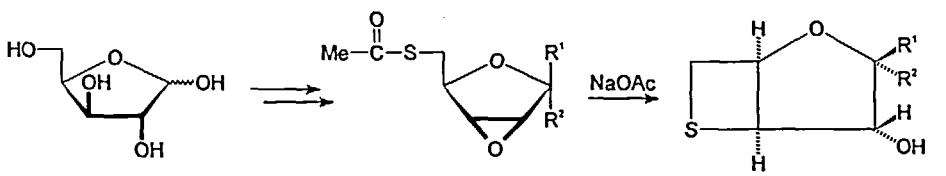
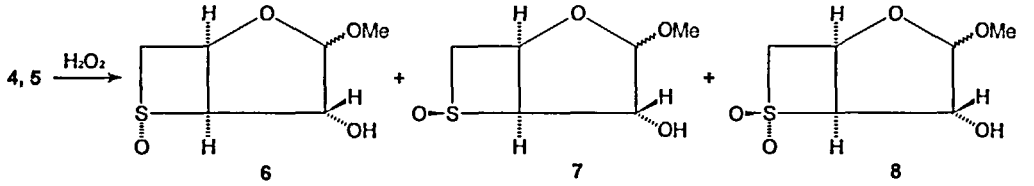
Abstract: The preparation of the two diastereoisomeric 3-methoxy-2-oxa-6-thiabicyclo-[3.2.0]heptan-4-ols **4** and **5** from D-xylose **1** *via* methyl 2,3-anhydro-α-D-ribofuranoside and the corresponding β-anomer is described. Oxidation of **4** and **5** yields the sulfoxides **6** and **7** and the sulfones **8**. – On the other hand, the two diastereoisomeric 3-methoxybicyclo[2.2.1]heptan-7-ols **11** and **12** are obtained from methyl 5-acetylthio-5-deoxy-2-*O*-mesyl-D-xylofuranosides **9** and **10** *via* Mitsunobu reaction and intramolecular cyclization. – The stereoisomeric counterparts of **4** and **5**, **13** and **14**, are obtained in only four steps from L-arabinose.

Starting from D-xylose **1** the two oxathiabicyclo[3.2.0]heptan-4-ols **4** and **5** were prepared in a multistep synthesis *via* Mitsunobu reaction and intramolecular cyclization of the thioacetates **2** and **3**. The two bicyclic compounds were obtained with good overall-yields as pure crystalline diastereoisomers. The structures of **4** and **5** were established by NMR spectroscopic methods and confirmed by X-ray structural analyses. The thietane ring of the β-isomer **5** turned out to be very flat (2.9°) whereas in the α-isomer **4** the angle was 16.5°.

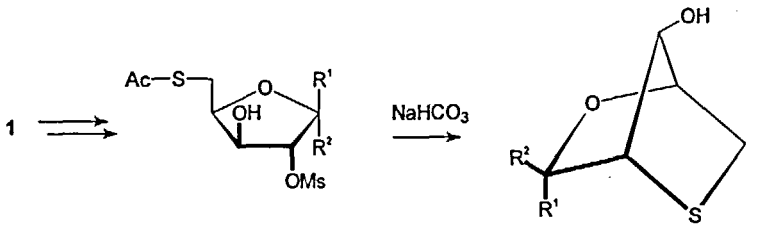


1 **2** $R^1 = H, R^2 = OMe$ **4**
3 $R^1 = OMe, R^2 = H$ **5**

Oxidation of **4** and **5** with hydrogen peroxide yielded the corresponding sulfoxides **6** and **7** as well as the sulfones **8**. The β-isomer of **8** exhibits a nearly planar thietane S,S-dioxide ring (2.0°) according to an X-ray structural analysis.



In a different way but using again the Mitsunobu reaction and cyclization of the thioacetates **9** and **10** we obtained the isomeric 2-oxa-5-thiabicyclo[2.2.1]heptan-7-ols **11** and **12** from the same precursor D-xylose **1**.



9 $R^1 = H, R^2 = OMe$ **11**
10 $R^1 = OMe, R^2 = H$ **12**

Starting from inexpensive L-arabinose it is also possible to prepare in only four steps two further diastereomeric 2-oxa-6-thiabicyclo[3.2.0]heptan-4-ol derivatives, the mesylates **13** and **14**. Once more, the Mitsunobu and the intramolecular cyclization reaction are applied.