

Preliminary communication

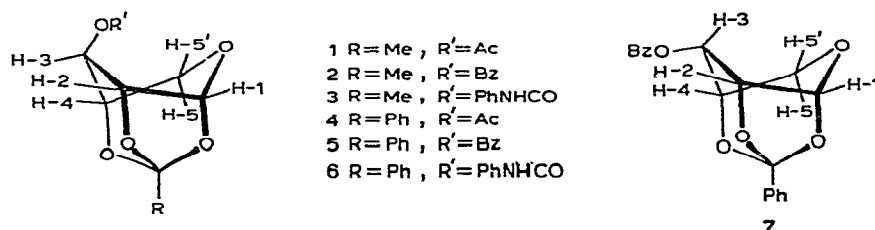
Rigid conformation of tricyclic orthoesters of sugars

A.F. BOCHKOV, V.M. DASHUNIN, A.V. KESSENIKH, N.K. KOCHETKOV, A.D. NAUMOV, and I.V. OBRUCHNIKOV

N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of U.S.S.R., Moscow B-334 (U.S.S.R.)

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Although a rigid conformation may be postulated for tricyclic orthoesters of sugars on the basis of general stereochemical considerations, there has previously been little experimental evidence to support this proposition. We have now synthesised the series of α -D-xylopyranose tricyclic orthoesters (1–6) and have investigated their p.m.r. spectra*; Coxon¹ recently described the p.m.r. spectrum of the C-3 epimer of compound 5, namely, 3-O-benzoyl- α -D-ribofuranose 1,2,4-orthobenzoate (7). Our results, together with those of Coxon, provide evidence for the high conformational rigidity of the heterocyclic skeleton of compounds 1–7.



The values of the ¹H spin–spin coupling constants obtained for orthoesters 1–6, for solutions in deuteriochloroform or benzene, and the data of Coxon¹ for orthoester 7 are presented in Table I. As can be seen, the variations of the substituent at position 3 of the xylose orthoesters, the change of solvent, and inversion of the configuration at C-3 do not significantly affect the coupling constants (excluding the obvious changes in H-3 coupling due to change of configuration at C-3). The variations of dihedral angle for each pair of protons (see Table II), as calculated in accordance with the Karplus equation², are less than 5°. Moreover, these variations in the angles are probably due to the approximate character of the Karplus equation and/or to the experimental error in the determination of coupling constants. Our results show, therefore, that the dihedral angles in these com-

*Details of these compounds and measurements will be published later.

TABLE I
SPIN-SPIN COUPLING CONSTANTS (J) FOR THE PROTONS OF THE PYRANOID RING OF THE ORTHOESTERS 1-7

Compound	Values for J						
	1,2	2,3	3,4	4,5'	4,5	5,5'	2,4 3,5
1-6 ^a	4.5-4.8	2.0-2.4	4.4-5.0	3.8-4.0	0.5-1.0	11.6-12.0	2.0-2.4 0.5-1.0
Average ^b	4.7	2.1	4.7	3.9	0.8	11.7	2.1 0.7
7 ^c	5.22	3.58	1.33	4.09	0.27	11.7	2.45 -0.18

^aFor solutions in CDCl₃ or in C₆H₆ at 60 or 100 MHz. ^bAverage values of all the data obtained for orthoesters 1-6. ^cThe data of Coxon¹, for a solution in CDCl₃ at 100 MHz.

TABLE II
THE DIHEDRAL ANGLES CALCULATED, ACCORDING TO THE KARPLUS EQUATION², FROM THE J VALUES IN TABLE I FOR ORTHOESTERS 1-7

Protons	1,2	2,3 ^a	3,4 ^a	4,5'	4,5
Dihedral angles (°)	36.5-41.5	57.5-59.0	38.0-41.5	45.0-46.0	106.5-111.5

^aExcluding orthoester 7.

pounds are unaffected by (i) solvent, (ii) the size of the axial substituent on C-3, and (iii) inversion of configuration at C-3, indicating a system of high conformational rigidity. The rigidity of the tricyclic system in the orthoesters 1-7 makes the compounds interesting models for stereochemical and conformational investigations.

REFERENCES

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- 2 M. Karplus, *J. Chem. Phys.*, 30 (1959) 11.

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