

CONFIGURATIONAL ASSIGNMENT OF QUATERNARY CENTRES CONTAINING C-1,3
DITHIANYL BRANCHED CHAIN IN ALICYCLIC AND CARBOHYDRATE CHEMISTRY BY
 ^{13}C N.M.R. SPECTROSCOPY¹.

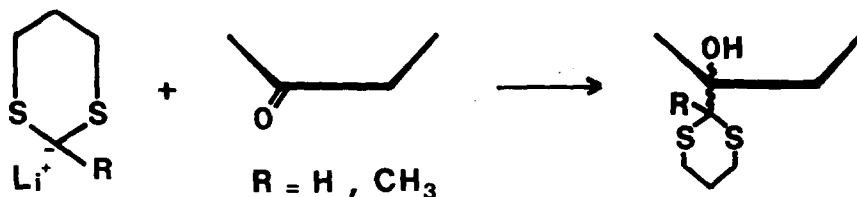
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There is much current interest in branched-chain sugars, components of miscellaneous antibiotics². The elegant method of nucleophilic acylation due to Corey and Seebach³ has recently been used for the synthesis of such compounds^{4,5}, including D-aldgarose⁶ a component of aldgamycin E.

In our laboratories^{4,6} the nucleophilic addition of 2-lithio-1,3-dithiane carbanions to keto-sugars has led to branched-chain carbohydrates with a new asymmetric centre (Figure) whose configurational assignment has hitherto presented serious difficulties.



It has been demonstrated recently that natural abundance ^{13}C N.M.R. spectroscopy is extremely useful for investigating stereochemical problems in carbohydrates⁷. We now report its use for assigning the configuration at quaternary centres.





Application of chemical shift theory⁸, single frequency off-resonance decoupling and comparison with the spectra⁹ of structurally related compounds especially 1 and 2 led to the assignments shown in the Table.

The configuration of the 1,3-dithian-2-yl residues in the conformationally rigid 1 and 2 can be assigned unequivocally from their ^{13}C N.M.R. spectra: the compound with the C-2' signal at 53.75 ppm, that is 7.2 ppm upfield of its epimer is assigned the configuration 1, with the dithianyl residue in an axial position.

It is interesting to note the relatively small chemical shift difference (1.4 ppm) between C-3 of 1 and 2. This indicates comparable 1,3 di-axial interactions in the two compounds.

From the position of the signal of C-2' of the dithian-2-yl moieties of compounds 3, 4 and 5 we assume these residues to be attached to the pyranose rings in an axial position.

TABLE
 ^{13}C N.M.R. Shifts⁹ of compounds (1)-(7)

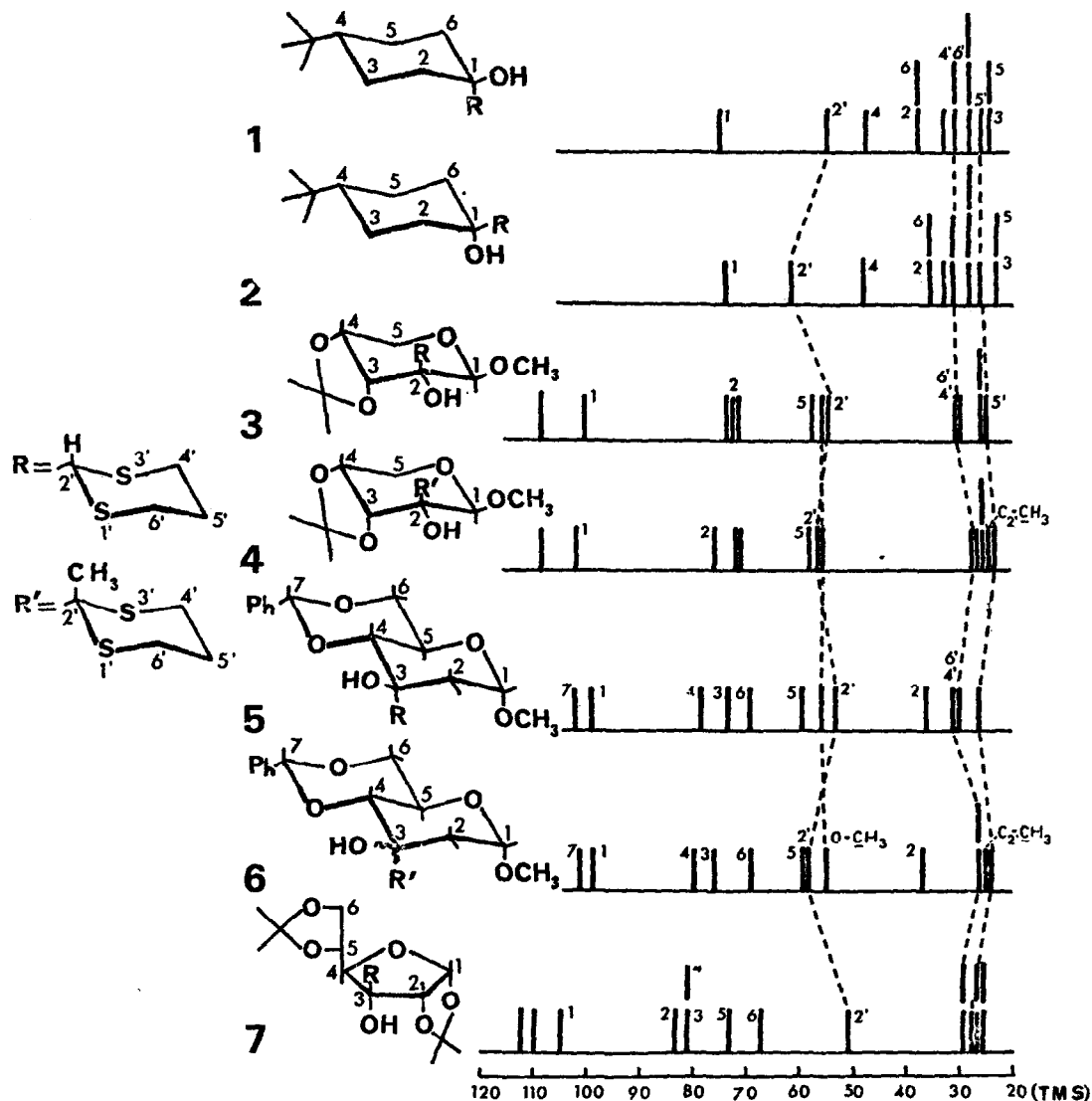
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	O-CH ₃		
1	73,80	35,95	23,65	46,60	23,65	35,95	-	-	31,85	27,20
2	73,15	35,05	22,25	47,37	22,25	35,05	-	-	32,15	27,40
3	99,80	72,05	70,80 ^a	72,95 ^a	57,30	-	-	55,45	-	-
4	101,40	75,40	71,10 ^a	71,55 ^a	57,85	-	-	55,05	-	-
5	98,50	35,80	72,85	78,00	59,25	69,05	101,65	55,25	-	-
6	98,40	36,35	75,65	79,85	59,15	68,85	100,90	54,70	-	-
7	104,45	83,20	80,50	80,50	73,05	67,95	-	-	-	-
			C-2'	C-4'	C-5'	C-6'	C ₂ -CH ₃	Aromatic C atoms		
								C _{subst.}	p-	o-,m-
1	-	-	53,75	29,90	25,15	29,90	-	-	-	-
2	-	-	60,95	30,55	25,70	30,55	-	-	-	-
3	108,20	25,45	54,70	29,80 ^a	24,80	30,30 ^a	-	-	-	-
4	108,20	25,55	55,80	26,55 ^a	24,05	26,95 ^a	25,15	-	-	-
5	-	-	53,10	30,10 ^a	25,80	30,65 ^a	-	137,25	128,80	126,15 127,95
6	-	-	58,50	26,00	24,15	26,00	24,90	137,00	128,30	125,70 127,55
7	109,60 112,20	25,35 26,35	50,50	29,10	26,75	29,10	-	-	-	-

^aValues within any horizontal column may be reversed.

The downfield position of the signal for C-2' of 6 did not permit an unambiguous assignment of the configuration of the substituents of C-3 in this case. Addition of the methyl group at C-2' in both 3 and 5 (to give 4 and 6 respectively) caused an upfield shift in the signals of C-4' and C-6' of about 4 ppm. The equatorial orientation, with respect to the dithiane ring, of the C-2—C-2' and C-3—C-2' bonds respectively in 3 and 5 is thus clearly demonstrated.

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Correlation of ^{13}C chemical shifts for the studied compounds

REFERENCES

1. Part (XI) in a serie on ^{13}C nmr analysis by G.L. *et al.* Part (X) E. Conway, R.D. Guthrie, S.D. Gero, G. Lukacs, A.M. Sepulchre, E.W. Hagaman and E. Wenkert, *Tetrahedron Letters* in the press .
2. S. Hanessian and T.H. Haskell, *The Carbohydrates* vol. II. A, Second Ed. Academic Press, p. 139 (1970); H. Grisebach and R. Schmid, *Angew. Chem. Internat. Edit.*, **11**, 159 (1972) ; U. Matern and H. Grisebach, *Eur. J. Biochem.*, **29**, 1 (1972).
3. E.J. Corey and D. Seebach, *Angew. Chem. Internat. Edit.*, **4**, 1075 (1965) ; D. Seebach, *Synthesis*, 17 (1969)

4. A.M. Sepulchre, G.Lukacs, G.Vass and S.D.Gero, Angew. Chem. Internat. Edit., 11, 148 (1972); A.M. Sepulchre, G. Vass and S.D. Gero, C.R.Acad.Sci. Paris, Ser.C, 274, 1077 (1972); A.M. Sepulchre, A. Gateau-Olesker, G. Lukacs, G. Vass, S.D. Gero and W. Voelter, Tetrahedron Letters, 3945 (1972).
5. H. Paulsen, V. Sinnwell and P. Stadler, Chem. Ber., 105, 1978 (1972)
6. A.M. Sepulchre, G. Lukacs, G. Vass, S.D. Gero and N.R. Williams, unpublished results.
7. (a) L.D. Hall and L.F. Johnson, Chem. Comm., 509 (1969); (b) A.S. Perlin et al Tetrahedron Letters, 2921, (1969); Canad. J. Chem., 48, 2596 and 2639 (1970); Carbohydrate Res., 15, 403 (1970); D.E. Dorman and J.D. Roberts, J. Amer. Chem. Soc., 92, 1355 (1970); (d) W. Voelter, E. Breitmaier, G. Jung et al., Angew. Chem. Internat. Edit., 10, 935 (1971); Chimia, 25, 168 and 362 (1971); 26, 138 (1972); Chem. Ber., 104, 1147 (1971); (e) D. Doddrell and A. Allerhand, J. Amer. Chem. Soc., 93, 2777 (1971); (f) E. Conway, R.D. Guthrie, S.D. Gero, G. Lukacs, A.M. Sepulchre, E.W. Hagaman and E. Wenkert, Tetrahedron Letters, in the press.
8. G.C. Levy and G.L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, 1972.
9. Spectra have been taken in CDCl_3 solution on a Bruker MFX 90 fourier transform spectrometer at 22, 63 MHz; chemical shift are given in parts per million down-field from TMS; $\int^{\text{TMS}} = \int^{\text{CDCl}_3} + 76,9 \text{ ppm.}$