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Note

Correlations between the sign of the D-line optical rotation and the absolute configuration of 1,1-bis(acylamido)-1-deoxyalditols

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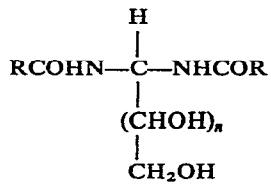
The rotatory power of acyclic derivatives of carbohydrates is usually very small because rotation about the carbon–carbon bonds allows a balance of the interactions which cause optical rotation. However, when the polyhydroxyl chain ends with a polarizable group, not only are the rotations larger than those of the parent compounds but it is possible also to make empirical correlations between the configurations of the asymmetric centres and the D-line rotations. The benzimidazole, phenylosotriazole, amide, and phenylhydrazide "rules" are examples of such correlations.

In this note, similar correlations are reported for 1,1-bis(acylamido)-1-deoxyalditols (**1**). These compounds



1 (R = Me, Et, or Ph)

are interesting because the molecular rotations are smaller than those of the aforementioned derivatives, and they do not have aromatic rings attached directly to the polyhydroxylated chain.

From the results given in Tables I and II, it is possible to state the following rules. (*a*) When the acyl group is acyclic (**1**, R = Me or Et), the compound will be dextrorotatory (in aqueous solution) if the configuration at C-2 is *S* (Cahn–Ingold–Prelog convention[1]); complete acetylation of the hydroxyl groups gives derivatives which do not follow the rule. (*b*) When a benzamido group is present (**1**, R = Ph), the substance having the uppermost asymmetric centre (C-2) belonging to the *S*-series will be levorotatory (in pyridine solution); acetylation or benzoylation of the hydroxyl groups produces derivatives which (in chloroform solution) follow the rule. (*c*) The absolute configuration of the other asymmetric centres do not influence significantly the sign of the D-line rotation.

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TABLE I

$[M]_D$ VALUES[a] OF 1,1-BIS(ACYLAMIDO)-1-DEOXYALDITOLS

No.	1,1-Bis(acylamido)-1-deoxyalditol derivative of	Configuration of C-2	Acyl group					
			Acetyl		Propionyl		Benzoyl	
			$[M]_D$ (degrees)	Ref.	$[M]_D$ (degrees)	Ref.	$[M]_D$ (degrees)	Ref.
1	L-Erythrose	*R*	−17.4	2			+ 44.5	15
2	D-Threose	*R*	−23.7	3			+ 5.8	15
3	L-Threose	*S*	+22.4	4				
4	D-Arabinose	*R*	−23.7	5	−27.2	14	+ 19.0	15
5	L-Arabinose	*S*	+22.0	6			− 19.3	15
6	5-Deoxy-L-arabinose	*S*	+43.6	7			− 7.5	16
7	5-*O*-Benzoyl-D-arabinose	*R*					+ 32.5	16
8	D-Lyxose	*R*	−23.0	4	−23.6	14	+ 17.1	15
9	5-*O*-Benzoyl-D-lyxose	*R*					+137.9	16
10	D-Ribose	*S*	+36.7	8			− 27.1	15
11	D-Xylose	*S*					− 8.2	15
12	D-Glucose	*S*	+10.4	9	+20.9	9	+ 6.0	17
13	6-*O*-Benzoyl-D-glucose	*S*					+ 32.0	22
14	D-Mannose	*R*	−38.6	10			+ 14.5	18
15	D-Galactose	*S*	+19.0	11			− 24.6	19
16	L-Rhamnose	*S*	+61.0	12			+ 55.9	20
17	D-*glycero*-D-*gulo*-Heptose	*S*	+22.6	13			− 48.6	13
18	D-*glycero*-L-*manno*-Heptose	*S*	+31.6	13			− 37.8	13
19	D-*glycero*-D-*galacto*-Heptose	*S*	+34.1	13			− 5.6	13

[a]Ro tations of acetamido or propionamido derivatives were measured in aqueous solution, and those of benzamido derivatives in pyridine.

TABLE II

[M]D VALUES[a] OF SOME FULLY *O*-ACYLATED 1,1-BIS(ACYLAMIDO)-1-DEOXYALDITOLS

No.	*1,1-Bis(acylamido)-1-deoxyalditol derivative of*	*Configuration of C-2*	*Acetamido derivatives*				*Benzamido derivatives*			
			O-*Acetylated*		O-*Benzoylated*		O-*Acetylated*		O-*Benzoylated*	
			$[M]_D$ (*degrees*)	*Ref.*	$[M]_D$ (*degrees*)	*Ref.*	[*M*] (*degrrees*)	*Ref.*	$[M]_D$ (*degrees*)	*Ref.*
1	L-Erythrose	*R*	− 76.8	7			+ 41.7	15		
2	D-Threose	*R*	+252.3	3	+583.6	4	+372.7	15		
3	L-Threose	*S*	−251.6	4	−585.2	4				
4	D-Arabinose	*R*	+303.1	21					+493.8	15
5	D-Ribose	*S*	+ 81.5	15			− 56.4	15		
6	D-Xylose	*S*					−273.2	15		
7	5-Deoxy-L-arabinose	*S*					−450.5	16		
8	5-*O*-Benzoyl-D-lyxose	*R*					+219.0	16	+308.9	16
9	5-*O*-Benzoyl-D-arabinose	*R*					+417.5	16		
10	D-Glucose	*S*	+103.4	9			−247.7	11		
11	D-Mannose	*R*							+233.8	10
12	D-Galactose	*S*	−184.2	11						
13	L-Rhamnose	*S*							−258.1	12
14	D-*glycero*-D-*gulo*-Heptose	*S*	+ 6.2	13			−121.4	13		
15	D-*glycero*-L-*manno*-Heptose	*S*	+ 89.4	13			+ 33.6	13		
16	D-*glycero*-D-*galacto*-Heptose	*S*	−139.2				−349.9	13		

[a]Rotations were measured for chloroform solutions.

Rule (*a*) is followed by all the samples (**1–18**) examined, but, in the case of the benzamido derivatives [rule (*b*)] three exceptions (parent sugars, **12**, **13**, and **16**; Table I) were found. In the case of the fully *O*-acylated benzamido derivatives, only one exception [the hexa-acetate of 1,1-bis (benzamido)-1-deoxy-D-*glycero*-L-*manno*-heptitol) was found.

O.r.d. and c.d. studies of these compounds are in progress to obtain a deeper insight on these correlations.

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