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Note

Chromatography of 1-deoxy-1-nitroalditols on a cation-exchange resin in the lanthanum form

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Chromatography of mixtures of sugars and alditols on cation-exchange resins, mainly as the alkaline earth metal forms, has been used often[1–4]. The lanthanum (La^{3+}) form is most efficient for alditols, since acyclic polyols are retained more strongly than the cyclic analogues[5–8]. The above cations form characteristic complexes with polyols[9–12] and result in different retention times. The problem of fractionating mixtures of at least three products, including two alditol derivatives, is encountered when the nitromethane synthesis is applied to aldoses. We have investigated the utility of the La^{3+} form for the resolution of mixtures of epimeric 1-deoxy-1-nitroalditols and for their separation from the parent aldoses.

The pairs of 1-deoxy-1-nitroalditols, formed on application of the nitromethane synthesis to D-galactose, D-glucose, and D-idose, could be resolved completely and separated also from the parent sugars (Table I). The resolutions for the products from D-arabinose, D-altrose, D-mannose, and D-talose were partial but utilisable for preparative purposes. For the other sugars, only separations of the parent aldoses from unresolved epimeric pairs of 1-deoxy-1-nitroalditols were observed.

Alditols that have an all-*gauche* arrangement of secondary hydroxyl groups in their planar zigzag conformations are retained most strongly on the La^{3+} form, whereas those with all-*trans* arrangements are retained least strongly. The other alditols, including those without any 1,3-parallel oxygen–oxygen interactions, have retention times between those of the preceding two categories. Similar trends were observed for 1-deoxy-1-nitroalditols, but the presence of the nitro group reduced the retention times (Table I). Thus, 1-deoxy-1-nitro-D-glucitol formed a stronger complex with La^{3+} ions than did the D-*manno* isomer. Epimeric pairs of 1-deoxy-1-nitroalditols from D-galactose and D-altrose exhibited similar behaviour. Moreover, the observed order of elution, *e.g.*, 1-deoxy-1-nitro-D-glucitol, 6-deoxy-6-nitro-L-glucitol, and D-glucitol, reflected the influence of the nitro group on the *xylo* complexing site. Thus, the nearer the nitro group was to the site of complexation, the bigger the effect in reducing complexation.

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TABLE I

Resolutions and relative retention volumes of 1-deoxy-1-nitroalditols and parent aldoses[a]

Polyol	R_S	$R_{P,A}$	R_{PE}	$R_{G\text{-}ol}$
D-Arabinose	0.5	1.0	0.64	0.22
1-Deoxy-1-nitro-D-mannitol	0.9	1.3	0.80	0.28
1-Deoxy-1-nitro-D-glucitol		2.2	1.4	0.49
D-Lyxose	0.8	1.0	0.85	0.30
6-Deoxy-6-nitro-D-altritol	<0.4	1.2	1.0	0.36
1-Deoxy-1-nitro-D-galactitol		1.3	1.1	0.40
D-Ribose	2.2	1.0	2.4	0.65
1-Deoxy-1-nitro-D-allitol	<0.4	0.36	0.88	0.25
1-Deoxy-1-nitro-D-altritol		0.36	0.88	0.25
D-Xylose	4.1	1.0	0.64	0.23
6-Deoxy-6-nitro-L-glucitol	<0.4	3.1	2.1	0.72
1-Deoxy-1-nitro-D-iditol		3.1	2.1	0.72
D-Allose	0.6	1.0	0.99	0.35
1-Deoxy-1-nitro-D-*glycero*-D-*allo*-heptitol	<0.4	0.82	0.82	0.29
1-Deoxy-1-nitro-D-*glycero*-D-*altro*-heptitol		0.82	0.82	0.29
D-Altrose	0.8	1.0	0.68	0.24
1-Deoxy-1-nitro-D-*glycero*-D-*manno*-heptitol	0.8	1.4	0.97	0.34
1-Deoxy-1-nitro-D-*glycero*-D-*gluco*-heptitol		2.3	1.6	0.55
D-Galactose	1.5	1.0	0.63	0.22
7-Deoxy-7-nitro-L-*glycero*-L-*galacto*-heptitol	1.4	1.8	1.1	0.40
7-Deoxy-7-nitro-D-*glycero*-L-*galacto*-heptitol		3.8	2.4	0.82
D-Glucose	2.4	1.0	0.60	0.21
7-Deoxy-7-nitro-D-*glycero*-L-*gulo*-heptitol	1.0	3.1	1.8	0.67
1-Deoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol		4.8	2.8	1.0
D-Gulose	2.2	1.0	0.91	0.33
7-Deoxy-7-nitro-L-*glycero*-L-*gluco*-heptitol	<0.4	2.0	1.8	0.65
1-Deoxy-1-nitro-D-*glycero*-L-*galacto*-heptitol		2.6	2.4	0.86
D-Idose	4.3	1.0	0.64	0.23
1-Deoxy-1-nitro-D-*glycero*-L-*gulo*-heptitol	1.5	3.2	2.1	0.75
1-Deoxy-1-nitro-D-*glycero*-L-*ido*-heptitol		5.0	3.2	1.2
D-Mannose	0.6	1.0	0.64	0.23
7-Deoxy-7-nitro-D-*glycero*-D-*manno*-heptitol	0.5	1.2	0.82	0.29
1-Deoxy-1-nitro-D-*glycero*-D-*galacto*-heptitol		1.4	0.96	0.34
D-Talose	0.4	1.0	1.7	0.67
1-Deoxy-1-nitro-D-*glycero*-L-*allo*-heptitol	0.6	0.84	1.4	0.56
1-Deoxy-1-nitro-D-*glycero*-L-*altro*-heptitol		0.64	1.1	0.43

[a] On a column of a cation-exchange resin (La^{3+}) referred to the retention volume of the parent aldose (R_{PA}), pentaerythritol (R_{PE}), and D-glucitol ($R_{G\text{-}ol}$); R_S values are resolutions of pairs of epimeric 1-deoxy-1-nitroalditols or a 1-deoxy-1-nitroalditol and its parent aldose.

Although D-glucitol and L-iditol were resolved[5], the epimeric pair of 1-deoxy-1-nitro products derived from D-xylose was not resolved (Table I). Moreover, the order of elution observed for 1-deoxy-1-nitroalditols obtained from D-glucose and D-talose was not that expected. These results may reflect the *gauche* effect of the nitro group[13], observed in crystalline 2,6-anhydro-1-deoxy-1-nitroheptitols[14] and in a solution of 7-deoxy-7-nitro-D-*glycero*-L-*galacto*-heptitol hexa-acetate in chloroform[15], which prompted the conclusion that the "conformation in which the hydrogen atoms in the O_2NCH_2–CHOAc–end segment are all *gauche* is more populated". Another effect could be the preponderance of sickle conformations of acyclic polyols with 1,3-parallel oxygen–oxygen interactions[15,16]. Hence, a terminal nitro group probably influences both neighbouring and other hydroxyl groups, and thus affects the complexation with La^{3+} ions dramatically. An exact explanation of these exceptions will require a more detailed study.

EXPERIMENTAL

Mixtures of epimeric pairs of 1-deoxy-1-nitroalditols were prepared by an established general procedure[17]. Chromatography was performed on a column (0.9 × 90 cm) of Dowex 50W-X8 (La^{3+}) resin (200–400 mesh) by elution with degassed water at 18 mL/h. A closed system was used that involved a peristaltic pump (VCM 150, Czechoslovak Academy of Sciences), a six-way valve[18], a packed column, and a differential refractometer (Knauer 5100). Resolution (R_S) of pairs of polyols was calculated from the equation $R_S = 2(t_2 - t_1)/(w_1 + w_2)$, where t_1 and t_2 are retention times and w_1 and w_2 are the widths of the peaks. ^{13}C-N.m.r. spectra (internal MeOH) were recorded with a Bruker AM-300 spectrometer at room temperature. Individual 1-deoxy-1-nitro derivatives or their mixtures were identified by their transformation to the corresponding aldoses[17] and/or by comparison of their ^{13}C-n.m.r. spectra with published data[19].

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