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Note

Periodate oxidation of allitol: formation of ribose as an initial product

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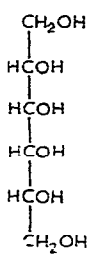
The hexitol allitol (**1**) is a major carbohydrate component of *Itea* plants[1,2], and biosynthetic studies[3] involving the incorporation of specifically ^{14}C-labelled D-glucose and D-fructose into the leaves necessitated a scheme for the degradation of allitol in order to determine the distribution of ^{14}C within the molecule. The method of periodate oxidation was adopted for this purpose, and a rate study of the reaction was carried out to determine optimal conditions for complete oxidation of the alditol. Previous studies of the periodate oxidation of various hexitols have indicated that slightly alkaline conditions are to be preferred; thus, at pH 7–8, D-mannitol, galactitol, and D-glucitol were oxidised completely within 1 h, whereas these hexitols gave low yields of formaldehyde[4] under unbuffered conditions.



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The periodate oxidation of allitol in phosphate buffer at pH ~7 resulted in an initially rapid consumption of 4 mol. of periodate followed by a subsequent slow reaction. The time taken for oxidation with 4 mol. of periodate varied with the conditions, being within 15 min when 0.05M periodate (20°, 30°) or 0.01M periodate at 30° was used, whereas ~1 h was required when 0.01M periodate at 20° was

employed. The subsequent consumption of the fifth mol. of periodate required ~4 h when the higher concentration of reagent was employed, but was considerably more prolonged (more than 24 h at 20°) with 0.01M periodate.

During the iodimetric determination of periodate in the above allitol oxidations, it was noticed that, with aliquots taken early in an experiment, the blue colour of iodine–starch gradually returned and increased in intensity after an end-point had been reached. This kind of behaviour was also noticed by Barker and Shaw[5] during a study of the periodate oxidation of D-ribose and related polyols; they also observed that an initially rapid consumption of 1 mol. of periodate was followed by a subsequent slow oxidation, a similarity to the present findings with allitol. To explain their results, Barker and Shaw suggested that ribose and periodate ion combine reversibly in equimolecular proportions to form a complex which can decompose to give oxidation products and iodate:

$$\text{Ribose} + IO_4^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{Complex} \xrightarrow{\text{slow}}$$

$$\text{First oxidation product} \xrightarrow[\text{(fast)}]{IO_4^-} \text{H.CHO} + \text{H.COOH}.$$

The formation of a ribose–periodate complex was shown to be characteristic of compounds possessing a *cis,cis*-1,2,3-triol system in a six-membered ring. The behaviour was not observed with ribitol, 5-*O*-triphenylmethyl-D-ribose, or 5-*O*-methyl D-ribose, thus, seemingly, excluding acyclic or five-membered ring systems.

To gain information on the initial stage in the periodate oxidation of allitol, the polyol was oxidised with various proportions of periodate for 1 h. Both allitol and ribose were detected in the products when either 1 or 2 molecular equivalents of periodate were used; 23% of the allitol was recovered unchanged in the former case when ribose was isolated as the toluene-*p*-sulphonylhydrazone in ~17% yield. When 6 molecular equivalents of periodate were used, no allitol could be detected in the products, although ribose was still present in small amounts as indicated by paper chromatography. These results indicated that ribose was the first product of the oxidation of allitol by periodate, and that the peculiarities mentioned above could be attributed to the subsequent complex formation and oxidation of the ribose. However, the recovery of unchanged allitol from reactions with 1 or 2 molecular equivalents of periodate suggested that allitol probably forms a complex similar to that of ribose with the periodate ion.

Schwarz[6] has investigated the products of reaction between other hexitols (D-mannitol, galactitol, and D-glucitol) and 0.1 molecular equivalent of periodate, and showed that in each case preferential attack on *threo*-glycol groups occurred. This observation agrees with the fact that, in the staggered conformation, *threo*-glycol groups are in fact *cis* to each other and would therefore be more susceptible to attack by the periodate ion *via* the formation of a cyclic intermediate[7]. Thus, mannitol was found to give mainly glyceraldehyde on oxidation with a limited quantity of periodate, and in no case was more than a trace of pentose found in the reaction products.

Cleavage of *threo*-glycol groups, both secondary, is therefore preferred to cleavage involving a primary hydroxyl group. From the results of the present work on allitol, it appears that, in the absence of *threo*-glycol groups, the latter reaction is itself preferred to cleavage of an *erythro*-glycol group of an acyclic polyol, since ribose was the main product in the oxidation of allitol with 1 molecular equivalent of periodate.

EXPERIMENTAL

General procedure. — Allitol, accurately weighed, was dissolved in a small quantity of water, and appropriate volumes of buffer solution (0.2M phosphate, pH 8) and aqueous sodium metaperiodate were added in that order. The solution was quickly made up to a known volume (usually 100 ml) and transferred to a dark-brown bottle. Aliquots (5 or 10 ml) were taken at regular intervals for analysis.

Determination of periodate consumed. — Periodate was determined according to the method described by Hough *et al.*[8,9]. An aliquot (5 or 10 ml, as convenient) of the reaction mixture was pipetted into a mixture of phosphate buffer (0.2M, pH 6.98, 25 ml) and 20% potassium iodide (2 ml). The liberated iodine was titrated immediately with sodium thiosulphate (0.01 or 0.05M, as convenient).

Allitol was oxidised under the following conditions: (*a*) 0.01M periodate (1.2 × theoretical) in 0.02M phosphate buffer at pH 7.5 → 7.0; (*b*) 0.05M periodate (3 × theoretical) in 0.04M phosphate at pH 7.0 → 6.7. The results are presented in Table I.

TABLE I

PERIODATE OXIDATION OF ALLITOL

Time (h)	*Periodate consumed (mol/mol of allitol)*			
	(a)[a]		(b)[a]	
	20°	*30°*	*20°*	*30°*
5 min	1.78	2.00	2.59	3.20
10 min	2.19	—	3.68	—
15 min	2.82	3.95	4.13	4.10
30 min	3.59	4.07	4.56	4.53
1	4.12	4.32	4.64	4.76
2	4.26	4.51	4.71	4.77
3	4.36	4.58	4.86	4.87
4	4.45	4.69	5.01	4.90
5	4.51	4.77	5.01	5.00
6	4.56	4.85	5.01	—
7	4.62	4.90	5.01	5.00
8	4.68	4.95	5.01	—
24	4.89	5.16	5.01	5.02

[a]See text for experimental conditions.

Products of periodate oxidation of allitol. — Allitol (0.2 mmol) was oxidised with different proportions of periodate in 0.04M phosphate buffer at pH 7. After 1 h, a slight excess of 0.5M barium acetate was added to remove any remaining periodate, and, after filtration, the solution was deionised by passing through a short column of mixed-bed ion-exchange resins [IR 120(H^+)/IR 45(^-OH)]. The eluate was concentrated to a syrup, and examined by paper chromatography (1-butanol–pyridine–water, 10:3:3) with detection by silver nitrate and *p*-anisidine hydrochloride spray-reagents. The syrup was then triturated with 70% ethanol to induce crystallisation of allitol, which had m.p. 149–150° after recrystallisation from aqueous ethanol (lit.[1] m.p. 149°). In some cases, the mother liquor was concentrated to a syrup that was heated under reflux (30 min) with methanol (2 ml) and toluene *p*-sulphonylhydrazine[10] (20 mg). Concentration to ~0.5 ml and cooling to 0° gave a solid product that was recrystallised from methanol to give ribose toluene-*p*-sulphonylhydrazone, m.p. 163–165°, having an infrared spectrum identical with that of an authentic specimen (m.p. 164°). The results are given in Table II.

TABLE II

PRODUCTS OF PERIODATE OXIDATION (1 h) OF ALLITOL

Proportion of sodium periodate (mol/mol of allitol)	*Carbohydrates detected[a] in reaction mixture*			*Recovery of allitol (%)*	*Yield[b] of ribose (%)*
	Allitol	*Ribose*	*Other*		
1	+	++	*t*	23	17
2	+	+++	*t*		
6	(−)	+	(−)	0	~0.2

[a]In increasing order of magnitude from visual examination of spots: +++, ++, +, *t* (trace), (−) absent. [b]Calculated from the yield of the toluene-*p*-sulphonylhydrazone.

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