

Table 1. Retention times ( $T$ -values) of methylated alditols, as their acetates, relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol.

Alditol	$T^a$	$T^b$
2,3,5-Tri- <i>O</i> -methyl-L-arabinitol	0.41	0.48
2,3-Di- <i>O</i> -methyl-L-arabinitol	1.07	—
2,4-Di- <i>O</i> -methyl L-arabinitol	1.10	1.40
2,3,4-Tri- <i>O</i> -methyl-D-xylitol	0.54	0.68
2,3-Di- <i>O</i> -methyl-D-xylitol	1.19	1.54
2,4-Di- <i>O</i> -methyl-D-xylitol	1.06	—
2-Mono- <i>O</i> -methyl-D-xylitol	2.15	—
3-Mono- <i>O</i> -methyl-D-xylitol	2.15	2.92
2,3,4,6-Tetra- <i>O</i> -methyl-D-glucitol	1.00	1.00
3,4,6-Tri- <i>O</i> -methyl-D-glucitol	1.83	1.98
2,4,6-Tri- <i>O</i> -methyl-D-glucitol	1.82	1.95
2,3,6-Tri- <i>O</i> -methyl-D-glucitol	2.32	2.50
2,3,4-Tri- <i>O</i> -methyl-D-glucitol	2.22	2.49
4,6-Di- <i>O</i> -methyl-D-glucitol	3.49	4.02
3,6-Di- <i>O</i> -methyl-D-glucitol	3.73	4.40
3,4-Di- <i>O</i> -methyl-D-glucitol	4.26	—
2,6-Di- <i>O</i> -methyl-D-glucitol	3.38	3.83
2,4-Di- <i>O</i> -methyl-D-glucitol	4.21	5.10
2,3-Di- <i>O</i> -methyl-D-glucitol	4.50	5.39
6-Mono- <i>O</i> -methyl-D-glucitol	5.0	—
3-Mono- <i>O</i> -methyl-D-glucitol	7.6	9.6
2-Mono- <i>O</i> -methyl-D-glucitol	6.6	7.9
2,3,4,6-Tetra- <i>O</i> -methyl-D-mannitol	0.99	1.00
2,4,6-Tri- <i>O</i> -methyl-D-mannitol	1.90	2.09
3,4,6-Tri- <i>O</i> -methyl-D-mannitol	1.82	1.95
2,3,4-Tri- <i>O</i> -methyl-D-mannitol	2.19	2.48
4,6-Di- <i>O</i> -methyl-D-mannitol	2.92	3.29
3,6-Di- <i>O</i> -methyl-D-mannitol	3.67	—
3,4-Di- <i>O</i> -methyl-D-mannitol	4.36	5.37
2,4-Di- <i>O</i> -methyl-D-mannitol	4.51	5.44
2,3,4,6-Tetra- <i>O</i> -methyl-D-galactitol	1.19	1.25
2,3,5,6-Tetra- <i>O</i> -methyl-D-galactitol	1.10	1.15
2,4,6-Tri- <i>O</i> -methyl-D-galactitol	2.03	2.28
2,3,5-Tri- <i>O</i> -methyl-D-galactitol	2.76	3.28
2,3,4-Tri- <i>O</i> -methyl-D-galactitol	2.89	3.41
3,4-Di- <i>O</i> -methyl-D-galactitol	5.5	6.93
2,6-Di- <i>O</i> -methyl-D-galactitol	3.14	3.65
2,4-Di- <i>O</i> -methyl-D-galactitol	5.1	6.35
2,3,4-Tri- <i>O</i> -methyl-L-fucitol	0.58	0.65
2,4-Di- <i>O</i> -methyl-L-fucitol	1.02	1.12
2-Mono- <i>O</i> -methyl-L-fucitol	1.43	1.67
2,3-Di- <i>O</i> -methyl-L-rhamnitol	0.92	0.98
3-Mono- <i>O</i> -methyl-L-rhamnitol	1.67	1.94

<sup>a</sup> 3 % OV-225 column. <sup>b</sup> 3 % ECNSS-M column.

tives and identified by GLC-MS. Transformation of the methylated sugars into alditol acetates was done as described earlier.<sup>1</sup>

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### Crystal Data on L-Tyrosine

ARVID MOSTAD, HANS MARTIN NISSEN  
and CHR. RØMMING

*Department of Chemistry, University of Oslo,  
Oslo 3, Norway*

Unit cell dimensions and space group of L-tyrosine have been reported by Khawas and Krishna Murti.<sup>1</sup> The determination was based on X-ray powder and fibre data, as single crystals could not be obtained by ordinary methods of crystallization.

Crystals suitable for single crystal X-ray experiments may, however, be obtained by recrystallization from a solution of oxalic acid in water. A concentrated solution of oxalic acid in cold water was heated with an excess of L-tyrosine and filtered. The solution was allowed to cool down to room temperature, and after a couple of weeks needle-formed crystals with an approximately square cross section appeared. Infrared spectra showed that the crystals are identical with the original compound and that the oxalate was not formed.

Oscillation and Weissenberg photographs proved the crystals to have orthorhombic symmetry. Systematic absent reflections are  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd; the space group is thus  $P2_12_12_1$ .

Unit cell parameters were determined using a Picker manual diffractometer with  $\text{CuK}\beta$  radiation ( $\lambda = 1.3922 \text{ \AA}$ ) and a take-off angle of  $0.5^\circ$ . Angular measurements were made for the eight symmetry related

reflections of each of five general reflections. Least squares calculations gave the following lattice parameters:

$a = 6.913(0.007)$  Å;  $b = 21.116(0.004)$  Å;  $c = 5.829(0.006)$  Å.

Figures in parentheses are estimated standard deviations.

The density of the crystals was measured by flotation to be  $1.41 \text{ g cm}^{-3}$ . The calculated density with four molecules per unit cell is  $1.414 \text{ g cm}^{-3}$ .

Khawas and Krishna Murti<sup>1</sup> concluded with a unit cell twice as large, the  $a$ -axis being  $13.89$  Å and  $b$  and  $c$   $21.08$  Å and  $5.84_2$  Å, respectively.

Intensity data have been collected with the use of an automatic Picker diffractometer. The crystal structure is presently being investigated using 2259 reflections observed above the background level.

1. Khawas, B. and Krishna Murti, G. S. R. *Acta Cryst. B* **25** (1969) 1006, 2663.

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## Acid Strengths of Mononaphthyl Phosphates

OSMO MAKITIE and SEIJA MIRTINEN

*Department of Chemistry, University of Helsinki, Helsinki 17, Finland*

In connection with studies of reactions of several phosphoric acids and esters in this laboratory, the values of the second dissociation constants of mononaphthyl phosphates ( $\text{C}_{10}\text{H}_7\text{OPO}_3\text{H}_2$ ) in aqueous potassium chloride solutions were determined potentiometrically. Both of these esters of orthophosphoric acid, 1-naphthyl phosphate and 2-naphthyl phosphate, are of interest in biochemical research and as analytical reagents.

The  $\text{p}K_2$  values  $5.848 \pm 0.005$  and  $5.762 \pm 0.003$  were obtained for the dissociation constants of 1-naphthyl and 2-naphthyl phosphates, respectively, at ionic strength 0.1 and  $25^\circ\text{C}$ . These values were evaluated by fitting the Debye-Hückel equation

$$\text{p}K_2 = \text{p}K_2^0 - 2.036 \sqrt{I}/(1 + \alpha\sqrt{I}) + B I$$

to experimental data obtained at various ionic strengths (0–2.0 M KCl).

Table 1. Values of the second dissociation constants of mononaphthyl phosphates in aqueous solution at  $25^\circ\text{C}$ . Titrant 0.1 M NaOH.

	$c_{\text{B}}:c$	pH	$\sqrt{I}$	$\text{p}K_2$
1-Naphthyl phosphate	0.280	5.695	0.105	6.064
$c = 4.002 \times 10^{-3}$ M	0.337	5.810	0.107	6.061
$\text{p}f_{\text{H}^+} = 0.044$	0.390	5.910	0.109	6.062
	0.445	6.010	0.111	6.064
	0.500	6.106	0.113	6.062
	0.555	6.199	0.114	6.060
	0.610	6.300	0.116	6.061
	0.665	6.401	0.118	6.058
	0.720	6.516	0.119	6.060
2-Naphthyl phosphate	0.279	5.617	0.108	5.986
$c = 4.190 \times 10^{-3}$ M	0.339	5.741	0.110	5.988
$\text{p}f_{\text{H}^+} = 0.045$	0.399	5.852	0.112	5.987
	0.430	5.906	0.113	5.985
	0.489	6.016	0.115	5.990
	0.520	6.067	0.116	5.987
	0.590	6.190	0.118	5.987
	0.652	6.303	0.120	5.985
	0.714	6.430	0.122	5.987

Illustrative titration data are shown in Table 1. The computed values of the thermodynamic constants and the parameters of the Debye-Hückel equations are listed in Table 2.

The mononaphthyl phosphates are clearly stronger acids than orthophosphoric acid itself. The 2-naphthyl ester seems also to

Table 2.  $\text{p}K_2$  values of mononaphthyl phosphates at  $25^\circ\text{C}$ .

	$I$	$\text{p}K_2$	$\alpha$	$B$
1-Naphthyl phosphate	Zero	6.27	1.51	0.10
	0.1	5.85		
	1.0	5.57		
2-Naphthyl phosphate	Zero	6.19	1.52	0.10
	0.1	5.76		
	1.0	5.48		