

TARTARIC ACID AND ITS *O*-ACYL DERIVATIVES.

7. CRYSTAL STRUCTURE OF *O*-*p*-ANISOYL-D-TARTARIC

ACID AND ITS DIMETHYLAMMONIUM SALT TRIHYDRATE

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Monoacylated derivatives *O*-*p*-anisoyl-D-tartaric acid and its *N,N*-dimethylammonium salt are synthesized by the partial hydrolysis of *O,O'*-di-*p*-anisoyl-D-tartaric acid. Crystal and molecular structures of both compounds have been determined and analyzed. In both of them, some strong and moderate strength [O...H...O] hydrogen bonds exist between the carboxylic units. The intermolecular hydrogen bonds link the adjacent fragments forming infinite one-dimensional chains parallel to the X-axis.

Keywords: tartaric acids, acyl derivatives, anisoyl.

INTRODUCTION

Tartaric acid acyl derivatives have wide applications in the chemical and pharmaceutical industry [1-3]. Monoacyltartaric acid derivatives are applied as ligands in chiral (acyloxy) boranes (CAB) [4-6], catalysts for Diels-Alder [5, 7] and asymmetric aldol condensation [1, 8] reactions. The aim of this work is to obtain *O*-*p*-anisoyl-D-tartaric acid (**B**) using the method based on partial hydrolysis and to confirm the structures of pure *O*-*p*-anisoyl-D-tartaric acid (**B**) and its salt (**A**) by the X-ray structural analysis. This contribution continues our research focused on the determination and analysis of the crystal structures of tartaric acid derivatives [9].

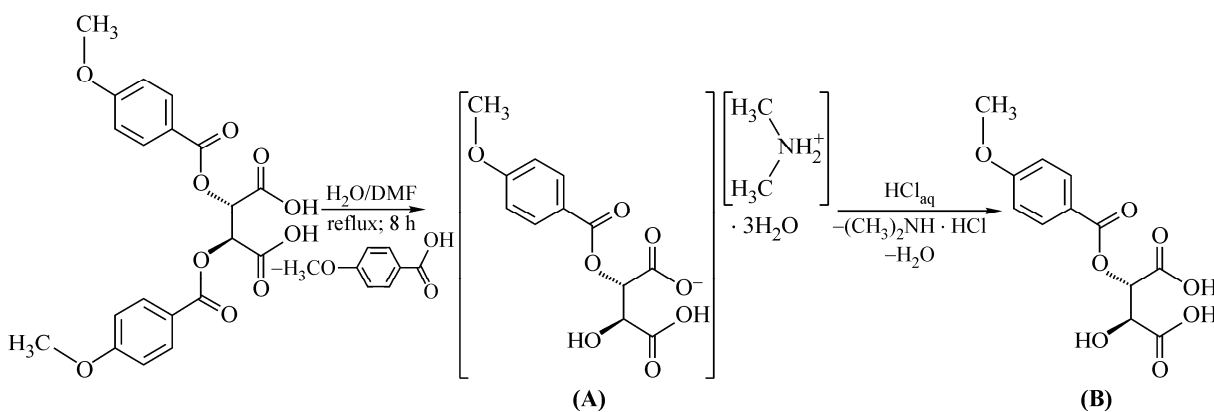
EXPERIMENTAL

Optical rotation was determined with Polarimetr PolAAR 32. Elemental analysis was carried out with Perkin Elmer PE II CHNS/O. ¹H NMR spectra were measured on Merkury 400 MHz in (D₆)DMSO; chemical shifts δ are in ppm relative to SiMe₄. The IR spectrum (KBr pellet) was recorded on Specord M80. Single crystal X-ray measurements for **A** and **B** were performed on a Kuma KM4CCD k-axis diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Only ω scans were taken into account. The multi-scan absorption correction was used. The solution and refinement were made using the SHELX package [10]. Most important crystal parameters and structural details are included in Table 1. In the **A** structure, C-type alert from *checkcif* stands for the disordered acidic H-atom ADPs. CCDC 803688 & 803689 contains the supplementary crystallographic data (CIF files) for this paper (for compounds **A** and **B** respectively). They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the authors.

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TABLE 1. Selected Crystal Data and Refinement Details for **A** and **B**

Experimental details	A	B
Chemical formula	$[\text{C}_2\text{H}_8\text{N}]^+[\text{C}_{12}\text{H}_{11}\text{O}_8]^-[\text{3H}_2\text{O}]$	$\text{C}_{12}\text{H}_{12}\text{O}_8$
M_r	383.35	284.22
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$
Cell parameters: $a, b, c, \text{\AA}$	7.4917(6), 8.0304(5), 30.8271(19)	7.7087(3), 5.6236(2), 14.9159(6)
$\alpha, \beta, \gamma, \text{deg}$	90.000, 90.000, 90.000	90.000, 94.043(3), 90.000
$V, \text{\AA}^3$	1854.6(2)	645.00(4)
Z	4	2
$d_x, \text{mg}\cdot\text{cm}^{-3}$	1.373	1.463
Crystal form, colour	Needle, colourless	Block, colourless
Crystal size, mm	0.11×0.15×0.46	0.20×0.36×0.49
$T_{\min}, T_{\max}$	0.9471, 0.9870	0.9410, 0.9753
No. of measured, independent, and observed reflections ($I > 2\sigma(I)$)	17289, 4434, 3637	5814, 2356, 2327
R_{int}	0.0279	0.0063
Θ_{max}	28.64	28.21
Range of h, k, l	$-10 \leq h \leq 10, -7 \leq k \leq 10, -41 \leq l \leq 41$	$-10 \leq h \leq 10, -7 \leq k \leq 6, -18 \leq l \leq 19$
$R[F^2 > 2\sigma(F^2)], wR(F^2), \text{GOOF}$	0.0268, 0.0570, 1.002	0.0214, 0.0573, 1.079
No. of reflections	2618	1626
No. of parameters	327	194
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}, \text{e}/\text{\AA}^{-3}$	0.220, -0.164	0.290, -0.142
CCDC No.	803688	803689

Scheme 1. Synthesis of *O*-*p*-anisoyl-D-tartaric acid *N,N*-dimethylammonium salt trihydrate (**A**) and pure *O*-*p*-anisoyl-D-tartaric acid (**B**)

RESULTS AND DISCUSSION

The synthesis of **A** and **B** is outlined in Scheme 1. The hydrolysis of *O,O'*-di-*p*-anisoyl-D-tartaric acid was carried out in the presence of DMF as an antifoaming agent, and unexpectedly, due to the parallel hydrolysis of DMF, resulted in the formation of *O*-*p*-anisoyl-D-tartaric acid *N,N*-dimethyl-ammonium salt trihydrate (**A**), M.p. 154-156°C. Elemental analysis calcd. for $\text{C}_{14}\text{H}_{25}\text{NO}_{11}$: C 43.7%, H 6.5%, N 3.7%, found: C 43.9%, H 6.6%, N 3.6%. ^1H NMR ((D_6)DMSO) δ : 2.440 (s, 6H, $\text{HN}(\text{CH}_3)_2$), 3.818 (s, 3H, OCH_3), 4.312 (d, $J = 4$ Hz, 1H, $\text{C}(\text{OH})\text{HCOOH}$), 5.256 (d, $J = 4$ Hz, 1H $\text{C}(\text{OOCAr})\text{HCOOH}$), 7.029 (d, $J = 8.8$ Hz, 2H, *o*- C_6H_4), 7.918 (d, $J = 8.8$ Hz 2H, *m*- C_6H_4). Pure *O*-*p*-anisoyl-D-tartaric acid (**B**) was obtained after

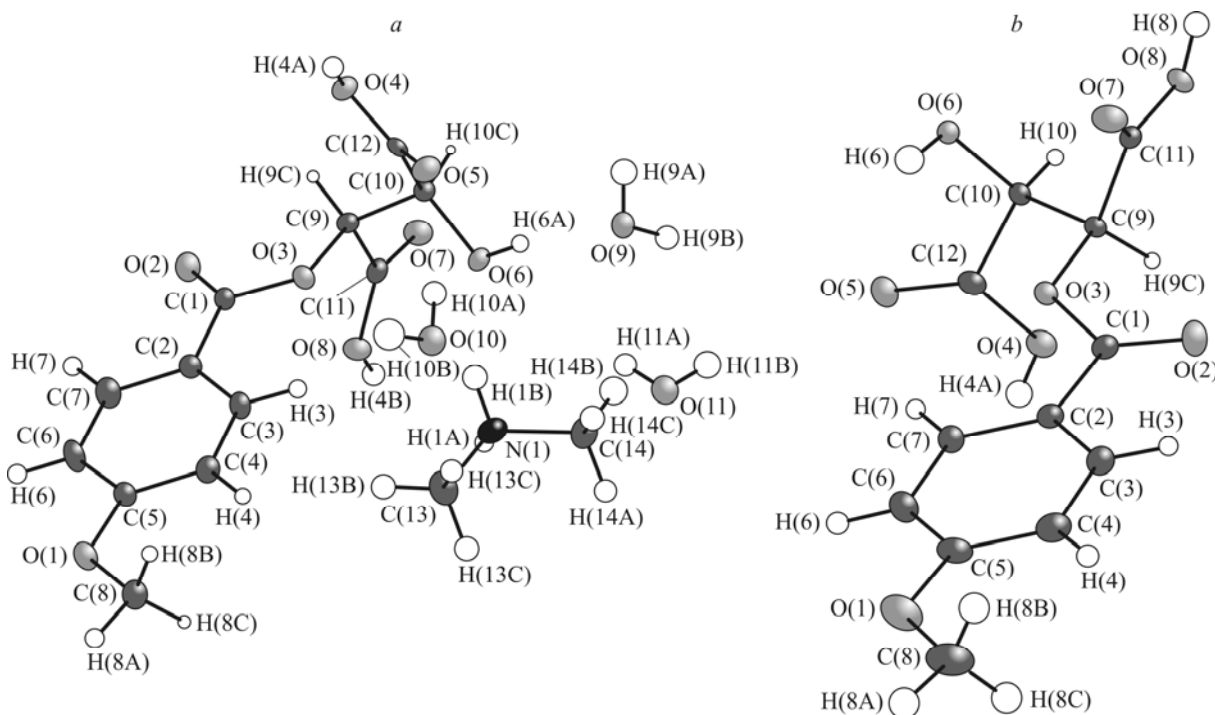


Fig. 1. Anisotropic displacement parameters (ADPs) and atom labeling in *O-p*-anisoyl-D-tartaric acid dimethylammonium salt trihydrate (*a*) and pure *O-p*-anisoyl-D-tartaric acid (*b*).

the acidification of **A** with hydrochloric acid. M.p. 191.3–195.2°C, $[\alpha] = +9.41$ $c = 1$ MeOH. Elemental analysis calcd. for $C_{11}H_{12}O_8$: C 50.7%, H 4.2%, found: C 50.62%, H 4.24%. 1H NMR ((D_6) -DMSO) δ : 3.834 (s, 3H, OCH_3), 4.643 (d, $J = 2.4$ Hz, 1H, $C(OH)HCOOH$), 5.418 (d, $J = 2.8$ Hz, 1H $C(OOCAr)HCOOH$), 7.063 (q, $J = 4.8$ Hz, 2H, o - C_6H_4), 7.985 (q, $J = 4.8$ Hz 2H, m - C_6H_4). IR (KBr) 3305 cm^{-1} , 1758 cm^{-1} , 1700 cm^{-1} , 1608 cm^{-1} , 1512 cm^{-1} , 1461 cm^{-1} , 1393 cm^{-1} , 1283 cm^{-1} , 1218 cm^{-1} , 1168 cm^{-1} , 1137 cm^{-1} , 1104 cm^{-1} , 1060 cm^{-1} , 1020 cm^{-1} , 924 cm^{-1} , 848 cm^{-1} , 768 cm^{-1} , 700 cm^{-1} , 665 cm^{-1} , 583 cm^{-1} , 508 cm^{-1} . Crystals of **A** and **B** were obtained by evaporation from an aqueous solution.

X-ray structural analysis of A. Dimethylammonium trihydrate salt of *O-p*-anisoyl-D-tartaric acid crystallises in the orthorhombic $P2_12_12_1$ space group with one *O-p*-anisoyl-D-tartaric anion, three water molecules, and one protonated *N,N*-dimethylamine moiety in the independent part of the unit cell (Fig. 1). The acid molecules are linked by a strong $O(8) \cdots H(4) \cdots O(4)$ hydrogen bond containing a disordered H-atom position occupied with the occupancy ratio *ca.* 0.6:0.4. The $D \cdots H \cdots A$ angles are 174.1(5)° and 177.0(7)°, and the $D \cdots A$ distance is 2.445(1) Å (Fig. 2). Intermolecular hydrogen bonds link the adjacent units together, thus forming infinite one-dimensional chains parallel to the X-axis. The aromatic fragments of the acid moieties interact by weak $C(4) \cdots H(4) \cdots O(2)$, and $C(7) \cdots H(7) \cdots C(8)$ (methoxy group) interactions parallel to the Y-axis of the crystal system.

The acid moieties interact by $C(6) \cdots H(6) \cdots O(4)$ interactions parallel to the Z-axis with the aromatic rings located on different neighbouring planes. Each chain of hydrogen bonds is additionally stabilized by $N(1) \cdots H(1A) \cdots O(5)$ and $N(1) \cdots H(1B) \cdots O(6)$ hydrogen bonds with the $D \cdots A$ distances and $D \cdots H \cdots A$ angles of 2.806(2) Å, 2.794(2) Å, 162.3(1)°, 160.1(2)° respectively. Chains formed by the acid molecules are parallel onetoanother, and they are bound by hydrogen bonds with water molecules.

X-ray structural analysis of B. Pure *O-p*-anisoyl-D-tartaric acid crystallises in the monoclinic space group $P2_1$ with one acid molecule in the asymmetric part of the unit cell. The molecular structure of the acid moiety is shown in Fig. 1. The acidic fragments form chains bound by moderately strong $O(1) \cdots H(1) \cdots O(5)$ hydrogen bonds. The $D \cdots H \cdots A$ angle is 161.9(2)° and the $D \cdots A$ distance is 2.70(1) Å (Fig. 2).

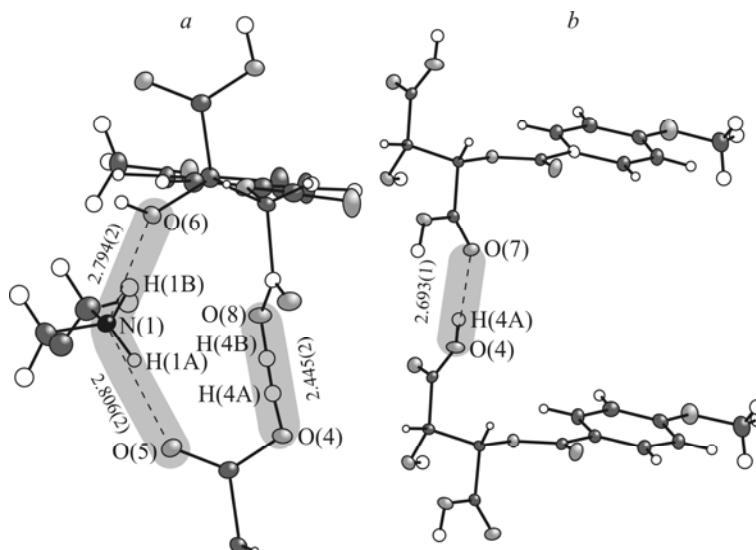


Fig. 2. (a) Strong hydrogen bonds existing between the acid moieties in the crystal structure of **A**, (b) moderate hydrogen bond in the acid **B** crystal structure.

The acid molecules maintain the same type of packing as in the structure of **A**. They form infinite one-dimensional chains of molecules parallel to the X-axis.

CONCLUSIONS

The presented report shows the synthesis of *O*-*p*-anisoyl-*D*-tartaric acid *N,N*-dimethylammonium salt trihydrate (**A**) and pure *O*-*p*-anisoyl-*D*-tartaric acid (**B**). Details of the crystallographic structures of **A** and **B** have been presented.

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