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# Structure of Potassium Hydrogen (+)-Tartrate at 100 K, $K^+.C_4H_5O_6^-$

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**Abstract.** $M_r = 188{\cdot}18$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}749\,(3)$, $b = 10{\cdot}582\,(3)$, $c = 7{\cdot}604\,(4)$ Å, $V = 623{\cdot}5\,(8)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}96$ g cm$^{-3}$ at room temperature according to van Bommel & Bijvoet [*Acta Cryst.* (1958). **11**, 61–70], $D_x = 2{\cdot}004$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 8{\cdot}2$ cm$^{-1}$, $F(000) = 384$, $T = 100\,(\pm 1)$ K, $R = 0{\cdot}0196$ for 1499 observed reflections. van Bommel & Bijvoet determined the structure of ammonium hydrogen tartrate and stated that potassium hydrogen tartrate has an isomorphous structure. The present study confirms that this is so and also confirms the absolute configuration postulated by them.

**Introduction.** In the history of crystallography the salts of tartaric acid have played a famous role in that they were the subject of the first studies of absolute configuration performed by Bijvoet and his group. The rubidium salt was the first compound for which an assignment of the enantiomer, based on experiment, was made. In contrast to a number of alkali salts of tartaric acid no structural data have so far been published for the optically active potassium salt. van Bommel & Bijvoet (1958) state that it is isomorphous with the ammonium salt. A description of the structure determination of the potassium salt is given in a crystallographic textbook by Luger (1980). The results of a low-temperature X-ray investigation of the title compound are now reported which are related to the ammonium hydrogen tartrate structure data.

**Experimental.** Platelet-like crystal, $0{\cdot}4 \times 0{\cdot}1 \times 0{\cdot}7$ mm, large faces (010) and $(0\bar{1}0)$. Automatic Siemens four-circle diffractometer, $\theta$–$2\theta$ scan mode. No transition detected on cooling. Crystal kept at constant low temperature of 100 K by two coaxial gaseous nitrogen streams generated by an apparatus which was designed and built in cooperation with Dietrich & Dierks (1970). Lattice constants determined from 14 high-order reflections. One octant ($hkl \geq 0$) of independent reflections measured, $\theta_{\max} = 35°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}807$ Å$^{-1}$, 1571 reflections of which 72 were classified as unobserved with $I < 2\sigma(I)$. Standard reflections 400 and 060 measured every 40 reflections, statistical intensity variation of 0·5%. Corrections for Lorentz–polarization and for absorption [program *ABSCOR* in *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); minimum absorption correction factor 1·088, maximum 1·348]. Room-temperature atomic parameters given by Luger (1980) were used as input parameters for refinement. Usual parameters, including an isotropic-extinction parameter, refined by full-matrix least squares using spherical scattering factors with complex anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974). Quantity minimized $\sum w(|F_o| - |F_c|)^2$, with $w = xy$, $x = 1$ for $\sin\theta > 0{\cdot}5$, $x = (\sin\theta)/0{\cdot}5$ for $\sin\theta \leq 0{\cdot}5$, $y = 1$ if $|F_o| < 13{\cdot}0$ and $y = 13{\cdot}0/|F_o|$ otherwise. Parameters for $w$ were chosen so as to make $w\Delta F$ almost independent of $|F_o|$ and $\sin\theta$. Unobserved reflections were included only if $|F_c| > |F_o|$. Extinction correction factor for the calculated structure factors $F_c(hkl)$ varied between 1·000 and 0·87. For observed reflections final $wR = 0{\cdot}024$ and $R = 0{\cdot}0196$. $(\Delta/\sigma)_{\max} = 0{\cdot}0002$ for non-hydrogen atoms, 0·001 for H atoms.

The absolute configuration was determined by parallel refinements of the two enantiomorphic forms with all reflections, reaching reliability indices of 0·022 and 0·027, defined by $R = [\sum_{\mathbf{h}} \big||F_o(\mathbf{h})| - k|F_c(\mathbf{h})|\big|]/\sum_{\mathbf{h}}|F_o(\mathbf{h})|$. Applying the Hamilton (1965) $R$ factor test, on the significance level of 0·005, clear preference was obtained for the configuration defined by the structure shown in the stereodiagram Fig. 1, which is the same as

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that given by van Bommel & Bijvoet (1958) for ammonium hydrogen tartrate as the probable absolute configuration. Their atom numbering is retained. Table 1 presents the final atomic parameters of potassium hydrogen (+)-tartrate at 100 K. The coordinates can be transformed to those of the ammonium salt according to $z + \frac{1}{4}, y + \frac{1}{4}, -x + \frac{5}{4}$.

Because of the use of spherical scattering factors the final difference Fourier map shows a number of residual density peaks of up to 0·38 e Å$^{-3}$. The three highest are near the middle of the three C—C bonds, the one near the central bond being markedly lower than the other two. Peaks next in height are between C—O bonds. Lower peaks, <0·21 e Å$^{-3}$, indicate oxygen lone pairs, especially one for each of the two hydroxy groups O(3)H(3) and O(4)H(4).*

**Discussion.** Intramolecular bond lengths are given in Table 2. They compare well with the results of van Bommel & Bijvoet (1958), as do the bond angles (deposited). The new angles involving H atoms are closer to 109·5°. The two C—C—O angles of the deprotonated carboxy group are equal at 117·6 (1)°, while for the other carboxy group they are 111·9 (1) and 123·5 (1)°. The temperature factor of the three bridging H atoms is about three times that of the two aliphatic H atoms. An interesting feature regarding the bond density is a displacement of the peak between C(2) and C(3), which appears to be pulled by the two nearest O atoms. The angle between the two least-squares planes of atoms O(1)O(2)C(1)C(2)O(3) and O(4)C(3)C(4)O(5)O(6) is 59·3 (25)°. In the crystal structure of (+)-tartaric acid, which was investigated by Okaya, Stemple & Kay (1966), this angle is 56·5 (17)°. This structure has a complicated three-dimensional network of O—H···O hydrogen bonds and shows the central C—C bond to be significantly longer than the other two.

The crystal lattice of the title compound is formed by layers of hydrogen-bonded tartaric anions separated by layers of K$^+$ cations. The above-mentioned large crystal faces are parallel to these layers and demonstrate the effectiveness of the hydrogen bonding. Each K$^+$ ion is surrounded by eight O atoms in a deformed cubic environment, the shortest K$^+$—O distance being 2·703 (1), the average 2·867 (1) Å. Each tartaric ion is engaged in six intermolecular O···O hydrogen bridges (Table 3) of which three are crystallographically independent, see also Fig. 1. Only one O atom, namely O(2), does not participate in the hydrogen bonding.

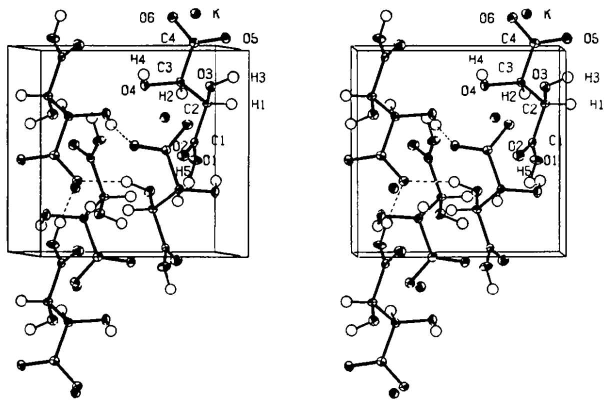

Fig. 1. Stereoview of the cell.

Table 1. *Atomic parameters* ($U_{eq}$ *and* $U$ *in* Å$^2$ × 10$^2$) *of potassium hydrogen* (+)*-tartrate at* 100 K

$U_{eq}$ values were calculated according to Hamilton (1959).

| | $x$ | $y$ | $z$ | $U_{eq}$ or $U$ |
|---|---|---|---|---|
| K$^+$ | 0·82765 (4) | 0·46756 (3) | −0·16517 (4) | 0·83 (1) |
| C(1) | 0·8596 (2) | 0·2405 (1) | 0·4628 (2) | 0·65 (3) |
| C(2) | 0·9228 (2) | 0·2307 (1) | 0·2739 (2) | 0·64 (3) |
| C(3) | 0·8100 (2) | 0·1362 (1) | 0·1739 (2) | 0·61 (3) |
| C(4) | 0·8757 (2) | 0·1286 (1) | −0·0157 (2) | 0·64 (3) |
| O(1) | 0·8835 (2) | 0·1346 (1) | 0·5501 (1) | 0·94 (3) |
| O(2) | 0·7927 (1) | 0·3352 (1) | 0·5246 (1) | 0·94 (3) |
| O(3) | 0·9197 (1) | 0·3509 (1) | 0·1889 (1) | 0·78 (2) |
| O(4) | 0·6328 (1) | 0·1681 (1) | 0·1865 (2) | 0·83 (2) |
| O(5) | 1·0320 (1) | 0·1029 (1) | −0·0387 (2) | 0·83 (2) |
| O(6) | 0·7691 (1) | 0·1524 (1) | −0·1387 (1) | 0·94 (3) |
| H(1) | 1·042 (3) | 0·196 (2) | 0·276 (3) | 0·1 (5) |
| H(2) | 0·825 (3) | 0·056 (2) | 0·231 (3) | 1·1 (6) |
| H(3) | 1·028 (4) | 0·360 (3) | 0·144 (4) | 3·5 (9) |
| H(4) | 0·619 (5) | 0·237 (3) | 0·136 (5) | 5 (1) |
| H(5) | 0·845 (4) | 0·146 (3) | 0·663 (4) | 2·6 (7) |

Table 2. *Bond lengths* (Å) *of the tartaric ion of potassium hydrogen* (+)*-tartrate at* 100 K *with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·524 (2) | C(4)—O(5) | 1·253 (2) |
| C(2)—C(3) | 1·531 (2) | C(4)—O(6) | 1·272 (2) |
| C(3)—C(4) | 1·532 (2) | C(2)—H(1) | 0·99 (2) |
| C(1)—O(1) | 1·314 (2) | C(3)—H(2) | 0·97 (2) |
| C(1)—O(2) | 1·223 (2) | O(3)—H(3) | 0·95 (3) |
| C(2)—O(3) | 1·423 (2) | O(4)—H(4) | 0·90 (4) |
| C(3)—O(4) | 1·417 (2) | O(1)—H(5) | 0·95 (3) |

Table 3. *The hydrogen bridges between tartaric residues of potassium hydrogen* (+)*-tartrate at* 100 K

| Bridge | O···O (Å) | ∠O—H···O (°) | O—H (Å) | H···O (Å) |
|---|---|---|---|---|
| O(1)—H(5)···O(6) | 2·532 (2) | 174·3 (40) | 0·95 (3) | 1·59 (3) |
| O(4)—H(4)···O(5) | 2·782 (2) | 165·7 (40) | 0·90 (4) | 1·90 (4) |
| O(3)—H(3)···O(6) | 2·735 (2) | 154·5 (40) | 0·95 (3) | 1·85 (3) |

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* Lists of observed and calculated structure factors, of anisotropic thermal parameters, and of bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39848 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of potassium hydrogen *meso*-tartrate was investigated by Kroon & Kanters (1972) with X-ray diffraction at 113 K and by Currie, Speakman, Kanters & Kroon (1975) with neutron diffraction. It is centrosymmetric, space group $P\bar{1}$ with two independent molecules in the asymmetric unit. As the *meso*-tartaric residues are dissymmetric, this structure is a racemate. It too shows a greater variety of intermolecular hydrogen bonds than the structure of the title compound. Two of the seven independent hydrogen bridges are symmetric across different inversion centres, connecting carboxy groups and having O···O distances of 2·483 (2) and 2·452 (2) Å. The one $K^+$ ion is surrounded by nine O atoms, the other by seven.

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# (–)-*cis*-2,8-Dimethyl-1,2,3,4,4a,9b-hexahydro-2*H*⁺-pyrido[4,3-*b*]indolium (*S*,*S*)-2,3-Di-*O*-benzoyltartrate(2–), $2C_{13}H_{19}N_2^+.C_{18}H_{12}O_8^{2-}$:A New Antiarrhythmic Drug

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**Abstract.** $M_r = 762\cdot9$, monoclinic, $C2$, $a = 17\cdot470$ (8), $b = 7\cdot975$ (1), $c = 14\cdot406$ (3) Å, $\beta = 94\cdot10$ (3)°, $V = 2002$ Å$^3$, $Z = 2$, $D_m = 1\cdot26$, $D_x = 1\cdot266$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·54178 Å, $\mu = 0\cdot82$ mm$^{-1}$, $F(000) = 812$, $T = 293$ K, final $R = 0\cdot034$ for 1252 unique observed reflections. The crystal structure consists of groups of three ions: two cations and one anion linked by hydrogen bonds. The groups possess crystallographic $C_2$ symmetry and are held together by van der Waals forces only. The saturated six-membered ring in the cation exists in a flattened chair conformation while the five-membered ring adopts a symmetric $C_s$ envelope conformation.

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**Introduction.** The title cation [hereafter (–)DB1021] is a new, structurally and chemically distinct, antiarrhythmic drug, whose site and mechanism of action are currently being investigated. It may exist in a number of geometrical conformational and optical isomers but only the present isomer has been found to be active. Of particular interest is, therefore, the detailed conformation and absolute configuration of the active (–)-enantiomer of DB1021.

**Experimental.** Single crystals obtained from an aqueous alcoholic solution of (–)DB1021 and (–)-(*S*,*S*)-2,3-di-*O*-benzoyltartaric acid (hereafter *S*,*S*-DBTA),