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Structure of *p*-Hydroxybenzoic Acid and *p*-Hydroxybenzoic Acid–Acetone Complex (2/1)

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Abstract. *p*-Hydroxybenzoic acid, $C_7H_6O_3$, M_r = 138.1, monoclinic, $P2_1/a$, a = 18.508 (7), b = 5.228 (2), c = 6.342 (3) Å, β = 93.22 (3)°, V = 612.7 (4) Å^3, Z = 4, D_m(295 K) = 1.525 (10), D_x = 1.497 (1) g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 0.11 mm^{-1}, F(000) = 288, T = 295 K, R = 0.041 for 1043 unique reflections. *p*-Hydroxybenzoic acid–acetone (2/1), $2C_7H_6O_3.C_3H_6O$, M_r = 334.3, monoclinic, $P2_1/a$, a = 24.093 (8), b = 7.232 (2), c = 9.699 (2) Å, β = 92.47 (2)°, V = 1688 (1) Å^3, Z = 4, D_m(294 K) = 1.308 (10), D_x = 1.315 (1) g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 0.11 mm^{-1}, F(000) = 704, T = 295 K, R = 0.054 for 2183 unique reflections. Pairs of *p*-hydroxybenzoic acid molecules form cyclic hydrogen-bonded dimers in the pure acid and in the acetone complex. The carboxyl H atom is disordered in the pure *para* isomer. The dimers are centrosymmetric in the pure acid and involve two crystallographically distinct molecules in the acetone complex. In the pure acid, the dimers are linked together through hydrogen-bonded phenolic groups; these bonds spiral around the twofold screw axes to make up layers of dimers parallel to (401). In the acetone complex, a pair of dimers is linked through hydrogen-bonded phenolic groups, and the acetone molecule is hydrogen bonded to one of the phenolic groups; these bonds spiral around the twofold screw axes to form chains of dimers approximately parallel to (201). The monoclinic *p*-hydroxybenzoic acid crystals appeared to be the lower temperature phase with a melting point of 488.0 (2) K and enthalpy of fusion (ΔH_f) of 30.99 (8) kJ mol^{-1}. In the calorimetric studies, a second peak was sometimes detected approximately 1 K above the melting point of the monoclinic *para* isomer. The structure of the high-temperature phase of *p*-hydroxybenzoic acid was not resolved; however, the high-temperature structure is expected to contain no dimers.

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Introduction. There is considerable interest in the structure and thermodynamic properties of the monosubstituted phenols owing to their technical importance. However, the crystallographic characterization of these compounds is incomplete, and the purity of the chemicals is often questionable since the data are quite old and since these compounds are notoriously difficult to purify, as they complex with many solvents and are easily oxidized (Ebisuzaki, Askari, Bryan & Nicol, 1987; Perrin, Armarego & Perrin, 1980). The crystal structure of *p*-hydroxybenzoic acid has not previously been reported (Steinmetz, 1914), although that of the monohydrate has been published (Colapietro, Domenicano & Marciante, 1979; Fukuyama, Ohkura, Kashino & Haisa, 1973). As part of our research on the monosubstituted phenols, we report on the structure of pure *p*-hydroxybenzoic acid and on the structure of the 2/1 acetone complex.

Experimental. Commercial *p*-hydroxybenzoic acid (Aldrich) was recrystallized several times and the solvent pumped off. Crystals of *p*-hydroxybenzoic acid employed in the melting experiment and in the structural study were grown both by vacuum sublimation from solid which had undergone six to eight previous sublimations, and from ethanol–*m*-xylene (1:1 to 1:20 ratio) solutions. Colorless crystals of *p*-hydroxybenzoic acid were grown from ethanol–xylene solution saturated at 313 K and slowly cooled. All crystals were stored in sealed Pyrex tubes.

A calibrated Perkin Elmer differential scanning calorimeter (DSC) (Ebisuzaki, Askari, Bryan & Nicol, 1987) was employed in searching for solid–solid phase transitions within the two instrument ranges (173–292 and 320–490 K) and for measuring the enthaply of fusion (ΔH_f). The two temperature ranges result from an instrument peculiarity, and the

range 292–320 K was not easily scanned. The melting points were determined on single crystalline samples melted in sealed capillary tubes, using a calibrated thermocouple and potentiometer (L & N K3). The error in the melting-point determination arose from visual observation.

Acetone (Fisher, certified ACS) was distilled twice from anhydrous $CaSO_4$ (Perrin, Armarego & Perrin, 1980). Clear columnar crystals of the 2/1 acetone complex were grown in a lidded flask by slowly cooling a warm saturated solution containing recrystallized *p*-hydroxybenzoic acid. Contact with atmospheric water was avoided. The acetone to hydroxybenzoic acid ratio of 0.520 (6):1 was found through weight loss resulting from acetone evaporation from the crystals of the complex, and supports the stoichiometry determined in the diffraction study.

Density measurements were conducted using the buoyancy technique (Bauer & Lewin, 1972).

The X-ray data were collected with a Nicolet $R3m/\mu$ four-circle automatic diffractometer. The X-ray source was Mo $K\alpha$ radiation used in conjunction with a graphite monochromator. The diffraction data were collected on a small sample ($0.15 \times 0.30 \times 0.32$ mm) of *p*-hydroxybenzoic acid cut from a large clear columnar crystal obtained in the sublimation process, while in the acetone complex, two separate samples ($0.65 \times 0.80 \times 0.83$ and $0.25 \times 0.45 \times 0.35$ mm) sealed in capillary tubes were employed. The lattice parameters of *p*-hydroxybenzoic acid were determined from 24 reflections ($8 < 2\theta < 26°$), while the parameters of the acetone complex were obtained from 19 reflections ($19 < 2\theta < 38°$). The intensities of the diffracted radiation were measured in a $\theta/2\theta$-scan mode for *p*-hydroxybenzoic acid and in an ω mode for the acetone complex, in the range of $3 < 2\theta < 56°$ for the hkl ranges $0 \le h \le 24$, $0 \le k \le 6$, $-8 \le l \le 8$ in *p*-hydroxybenzoic acid and $0 \le h \le 31$, $0 \le k \le 9$, $-12 \le l \le 12$ in the acetone complex. In *p*-hydroxybenzoic acid, the (401) reflection was too intense to be measured. For the larger sample of the acetone complex, eight of the strongest reflections were measured with the power to the tube reduced sixfold, owing to the absence of an attenuator; these reflections were $02\bar{1}$, 021, 112, $12\bar{1}$, 201, 211, $22\bar{1}$ and 311. Structure refinement improved with the removal of the eight strongest reflections from the diffraction data for the larger sample. From the diffraction data for the smaller acetone-complex sample, reflections $12\bar{1}$ and 201 were the most and second most intense reflections, respectively. Stationary background intensities were measured for half of the scan time on each side of a peak. For both crystals, two standard reflections were monitored every 48 reflections. The largest variation in the averaged intensity of the standard reflections was 2.2% for the pure acid and 5.8% for the acetone complex. A total of 1668 reflections were measured, but only 1043 with $F > 3\sigma(F)$ were used in the structure analysis of *p*-hydroxybenzoic acid, while in the acetone complex, 2183 reflections with $F > 4\sigma(F)$ from the total of 4665 in the merged diffraction data were employed. The Lorentz and polarization effects and the isotropic extinction parameter were corrected in both crystals. The isotropic extinction parameters were $1.3\,(3) \times 10^{-5}$ and $7.1\,(3) \times 10^{-6}$, respectively, for the uncomplexed acid and the complexed acid. No absorption corrections were made for either crystal since μ was 0.11 mm^{-1} for Mo $K\alpha$ radiation.

The structures were solved through the direct methods and difference Fourier synthesis of the *SHELXTL* program (Sheldrick, 1985). *SHELXTL* refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F) + gF^2]^{-1}$ and g was 0.0005 for *p*-hydroxybenzoic acid and 0 for the complex; $\sigma^2(F)$ was obtained from counting statistics. For the complex, $g = 0$ since the weighting minimized the effect of the strong reflections and the most intense reflections were excluded from the refinement. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). For the uncomplexed acid, electron density maps revealed the positions of all C and O atoms. For the complexed acid, the electron density map revealed the position of C and O atoms in the two *p*-hydroxybenzoic acid molecules; the C and O atoms in the acetone molecule were located in a difference Fourier map. Anisotropic thermal parameters were refined for C and O atoms. The H atoms were located through difference Fourier maps. Since refinement of coordinates and isotropic thermal parameters led to unreasonable values, all but four non-phenyl H atoms, in the acetone complex, were constrained to coordinates found in a difference Fourier map; in each methyl group, two H-atom positions were generated. Isotropic thermal parameters of the non-phenyl H atoms were constrained to 1.2 times that of the bonded atom, in the acetone complex. Totals of 120 and 250 parameters were refined, respectively, for the pure acid and the complex. Final values of R and wR were respectively 0.041 and 0.051 for the pure acid and 0.054 and 0.035 for the complex. The GOF and the largest Δ/σ values were 1.4 and 0.20, respectively, for hydroxybenzoic acid and were 2.2 and 0.05, respectively, for the complex. The largest and the smallest difference peaks were 0.19 and -0.13 e $Å^{-3}$ for the hydroxybenzoic acid and 0.18 and -0.24 e $Å^{-3}$ for the complex.

Discussion. *Thermodynamic data.* In approximately one half of the DSC scans of *p*-hydroxybenzoic acid

crystals obtained by sublimation, two transition peaks which differed by one degree were seen at the melting point. The area of the higher transition-point peak was usually 30–50% of that of the lower transition peak. In one half of the sublimed hydroxybenzoic acid samples, only one (melting) point, namely, the lower temperature (melting) phase could be observed. *p*-Hydroxybenzoic acid grown in ethanol–*m*-xylene solution more often consisted of one-phase crystals with one DSC peak. DSC scans of crystals of *m*-hydroxybenzoic acid, grown by vacuum sublimation, revealed two transition peaks similar to those observed in *p*-hydroxybenzoic acid, which differed by one degree near the melting point. The two peaks were associated with the two reported (Gridunova, Furmanova, Struchkov, Ezhkova, Grigor'eva & Chayanov, 1982) crystalline forms of *m*-hydroxybenzoic acid. In the present work, the orthorhombic *m*-hydroxybenzoic acid crystals were the higher temperature phase with a melting point of 474.0 (2) K with respect to the monoclinic *m*-hydroxybenzoic acid crystals which melted at 472.7 (2) K. In the monoclinic phase, pairs of *m*-hydroxybenzoic acid molecules form centrosymmetric hydrogen-bonded dimers, and the dimers are linked together through hydrogen-bonded phenolic groups (Gridunova, Furmanova, Struchkov, Ezhkova, Grigor'eva & Chayanov, 1982). Cyclic dimer formation is frequently seen in carboxylic acids (Leiserowitz, 1976). However, the orthorhombic *m*-hydroxybenzoic acid is an exception in that no dimers are formed. The dimerless orthorhombic *meta*-isomer phase consists of chains of molecules, and each *m*-hydroxybenzoic acid molecule is linked to two other molecules through hydrogen bonding with the phenolic group. The hydrogen bonding occurs between the phenolic group and the carbonyl group of a second molecule and between the same phenolic group and the carboxyl group of a third molecule (Gridunova, Furmanova, Struchkov, Ezhkova, Grigor'eva & Chayanov, 1982). From the above observations, we would like to suggest that the high temperature phase of *p*-hydroxybenzoic acid is also a dimerless phase as in *meta*-hydroxybenzoic acid. Unfortunately, we have not been able to separate the two phases in *p*-hydroxybenzoic acid for crystallographic studies.

A solid-state phase transition was observed in the *p*-hydroxybenzoic acid–acetone complex and in *p*-hydroxybenzoic acid monohydrate at 338 (5) K. At this gradual phase transition, the clear columnar crystals of the acetone complex and monohydrate turned chalky white. The transition enthalpy (ΔH) was 8 (2) kJ mol^{-1}; a typical value for solid–solid transitions (Ebisuzaki, Askari, Bryan & Nicol, 1987). No solid–solid transition was observed in the pure acid crystals.

The melting point of the low-temperature single-phase *p*-hydroxybenzoic acid was 488.0 (2) K and the enthalpy of fusion (ΔH_f) was 30.99 (8) kJ mol^{-1}, while the sealed acetone complex melted at 468 (1) K. In our previous study (Ebisuzaki, Askari, Bryan & Nicol, 1987), the constancy of ΔH_f and the melting point were found to be useful criteria for evaluating the crystal purity, especially when the compound complexes were solvents. One-phase crystals of *p*-hydroxybenzoic acid obtained from solution and from sublimation growth gave identical X-ray lattice parameters. The results of the elemental analyses presented below for *p*-hydroxybenzoic acid and for the acetone complex exclude the possibility of large amounts of impurity. The analyzed weight % of C, H and O are smaller than the calculated weight % for the acetone complex; this fact can be explained by the ease with which acetone evaporates during the handling process. Elemental analysis for $C_7H_6O_3$: found C 60.79, H 4.40, O (by difference) 34.81 wt%; calculated C 60.87, H 4.38, O 34.75 wt%. Elemental analysis for $C_{17}H_{18}O_7$: found C 58.28, H 4.73, O 32.34 wt%; calculated C61.07, H 5.43, O 33.50 wt%.

Crystal structures. Figs. 1 and 2 show the atom-numbering scheme in the pure acid and in the acetone complex, respectively. In the acetone complex, there are two crystallographically independent *p*-hydroxybenzoic acid molecules *A* and *B*. The atomic coordinates and thermal (m.s. displacement) parameters obtained from the diffraction data are listed in Table 1. Bond lengths and angles are given in Table 2.* Reasonable equivalent isotropic thermal (m.s. displacement) parameters were obtained for the atoms in the pure acid (Table 1). In the acetone complex, however, larger equivalent isotropic thermal (m.s. displacement) parameters of 0.1071 (14) and 0.120 (2) Å^2 were observed for the methyl C atoms C8 and C10, respectively, of the acetone molecule.

In both crystals, pairs of hydroxybenzoic acid molecules are linked through hydrogen bonds (2.635 Å pure acid, 2.614 Å complex) between carboxyl groups to form cyclic dimers as shown in Figs. 1–4. The dimers in the pure acid are centrosymmetric, while in the acetone complex, the dimers are formed from the independent molecules *A* and *B*. In Fig. 1 one sees a dimer of hydroxybenzoic acid with idealized positions of atoms H1 and H2, but the refined coordinates place four H atoms in the dimer.

* Lists of structure factors, anisotropic thermal (m.s. displacement) parameters, H-atom parameters, and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55218 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0372]

The refined coordinates of H atoms H1 and H2 are approximate sites of electron density. The ordering of the H atoms in the hydrogen bonds between the two molecules in *p*-hydroxybenzoic acid and *p*-hydroxybenzoic acid–acetone complex are different. In the *p*-hydroxybenzoic acid, the C—O bond lengths (C1—O1 and C1—O2) at 1.266 (2) Å are

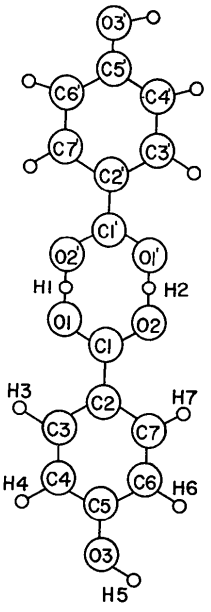

Fig. 1. The numbering of the atoms in the *p*-hydroxybenzoic acid dimer.

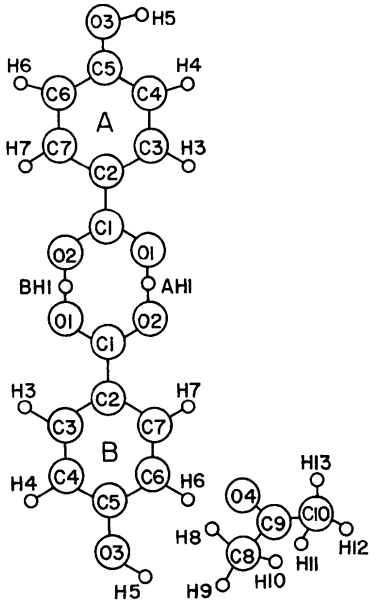

Fig. 2. The numbering of the atoms in the *p*-hydroxybenzoic acid–acetone complex.

Table 1. *Selected fractional atomic coordinates and equivalent isotropic temperature (m.s. displacement) factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
p-Hydroxybenzoic acid				
C1	0.94079 (8)	0.0501 (3)	0.2353 (3)	38.1 (5)
C2	0.89677 (8)	0.0816 (3)	0.4213 (2)	35.8 (5)
C3	0.90863 (9)	0.2852 (4)	0.5590 (3)	41.4 (5)
C4	0.86951 (9)	0.3085 (4)	0.7373 (3)	41.3 (5)
C5	0.81727 (8)	0.1286 (3)	0.7755 (2)	36.5 (5)
C6	0.80350 (9)	−0.0727 (4)	0.6383 (3)	39.2 (5)
C7	0.84385 (9)	−0.0963 (3)	0.4622 (2)	37.8 (5)
O1	0.98703 (7)	0.2203 (3)	0.1982 (2)	53.4 (5)
O2	0.93075 (7)	−0.1477 (3)	0.1223 (2)	51.2 (5)
O3	0.77883 (7)	0.1598 (2)	0.9534 (2)	47.8 (4)
p-Hydroxybenzoic acid–acetone				
*A*C1	0.05894 (9)	0.5937 (3)	0.2642 (2)	53.6 (9)
*A*C2	0.10769 (9)	0.5300 (3)	0.1915 (2)	48.9 (8)
*A*C3	0.10240 (9)	0.4537 (3)	0.0595 (2)	54.9 (8)
*A*C4	0.14888 (9)	0.3934 (3)	−0.0054 (2)	58.1 (9)
*A*C5	0.20090 (9)	0.4099 (3)	0.0593 (2)	53.1 (9)
*A*C6	0.20669 (9)	0.4866 (3)	0.1902 (2)	56.1 (9)
*A*C7	0.16031 (9)	0.5445 (3)	0.2554 (2)	53.2 (8)
*A*O1	0.01178 (6)	0.5905 (3)	0.1982 (2)	77.6 (7)
*A*O2	0.06439 (6)	0.6484 (2)	0.38665 (15)	69.6 (7)
*A*O3	0.24562 (7)	0.3479 (3)	−0.0089 (2)	71.9 (7)
*B*C1	−0.06674 (9)	0.7649 (3)	0.4575 (2)	56.1 (9)
*B*C2	−0.11506 (9)	0.8301 (3)	0.5307 (2)	50.4 (8)
*B*C3	−0.10946 (9)	0.9067 (3)	0.6620 (2)	53.8 (8)
*B*C4	−0.15477 (10)	0.9694 (3)	0.7291 (2)	55.2 (9)
*B*C5	−0.20748 (9)	0.9554 (3)	0.6661 (2)	57.7 (9)
*B*C6	−0.21372 (9)	0.8776 (4)	0.5353 (2)	70.6 (1.0)
*B*C7	−0.16797 (9)	0.8158 (4)	0.4692 (2)	63.9 (1.0)
*B*O1	−0.01945 (6)	0.7681 (3)	0.5239 (2)	75.7 (7)
*B*O2	−0.07223 (6)	0.7093 (2)	0.33522 (14)	74.4 (7)
*B*O3	−0.25422 (6)	1.0135 (3)	0.7258 (2)	83.4 (8)
C8	0.37724 (14)	0.2520 (4)	0.2903 (2)	107.1 (1.4)
C9	0.38724 (10)	0.3568 (4)	0.1632 (3)	71.6 (1.0)
C10	0.44596 (10)	0.3916 (4)	0.1288 (3)	120 (2)
O4	0.34949 (7)	0.4100 (3)	0.0886 (2)	91.7 (8)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

		p-Hydroxybenzoic acid–acetone	
	p-Hydroxybenzoic acid	Molecule *A*	Molecule *B*
C1—C2	1.480 (2)	1.470 (3)	1.467 (3)
C1—O1	1.266 (2)	1.280 (3)	1.284 (3)
C1—O2	1.266 (2)	1.253 (3)	1.254 (3)
C2—C3	1.386 (2)	1.395 (3)	1.391 (3)
C2—C7	1.385 (2)	1.391 (3)	1.387 (3)
C3—C4	1.382 (2)	1.379 (3)	1.371 (3)
C4—C5	1.380 (2)	1.382 (3)	1.389 (3)
C5—C6	1.381 (2)	1.387 (3)	1.390 (3)
C5—O3	1.377 (2)	1.364 (3)	1.355 (3)
C6—C7	1.383 (2)	1.373 (3)	1.374 (3)
C2—C1—O1	118.6 (2)	117.7 (2)	117.2 (2)
C2—C1—O2	118.2 (1)	120.0 (2)	120.5 (2)
O1—C1—O2	123.2 (2)	122.3 (2)	122.3 (2)
C1—C2—C3	120.8 (1)	121.4 (2)	121.6 (2)
C1—C2—C7	120.1 (1)	119.6 (2)	120.1 (2)
C3—C2—C7	119.1 (1)	119.0 (2)	118.3 (2)
C2—C3—C4	120.8 (2)	120.0 (2)	121.2 (2)
C3—C4—C5	119.2 (2)	120.2 (2)	119.9 (2)
C4—C5—C6	121.0 (2)	120.2 (2)	119.5 (2)
C4—C5—O3	117.5 (1)	118.1 (2)	123.4 (2)
C6—C5—O3	121.4 (1)	121.7 (2)	117.2 (2)
C5—C6—C7	119.2 (2)	119.5 (2)	120.0 (2)
C2—C7—C6	120.7 (2)	121.0 (2)	121.1 (2)
Acetone			
C8—C9	1.475 (4)	C8—C9—O4	121.4 (2)
C9—C10	1.489 (4)	C10—C9—O4	120.8 (2)
C9—O4	1.201 (3)	C8—C9—C10	117.7 (2)

equal and the angles (O2—C1—C2 and O1—C1—C2) at 118.2 (1) and 118.6 (2)° are also equivalent within the accuracy of the investigation. This equivalence suggests that the carboxyl H atom is disordered in the hydrogen bonds (O1–O2) (Leiserowitz, 1976) of hydroxybenzoic acid. Also the best structure refinement ($R = 0.041$ and $wR = 0.051$) was obtained by locating the H atoms using a site-occupancy factor of one half. In the dimer of the acetone complex, there are distinct bond-length differences between the double-bonded C=O lengths [1.253 Å for *A*(C1=O2) and 1.254 Å for *B*(C1=O2)] and the single-bonded C—O lengths [1.280 Å for *A*(C1—O1) and 1.284 Å for *B*(C1—O1)]. Furthermore, in the acetone complex (Fig. 2) the angles defined by the double-bonded C=O [*A*(C2—C1—O2) and *B*(C2—C1—O2)] are 120.3° while the angles defined by single-bonded C—O bonds [*A*(C2—C1—O1) and *B*(C2—C1—O1)] are 117.4°. These distinct bond lengths and angles indicate that the carboxyl H atoms, *A*H1 and *B*H1, are not disordered in the acetone complex.

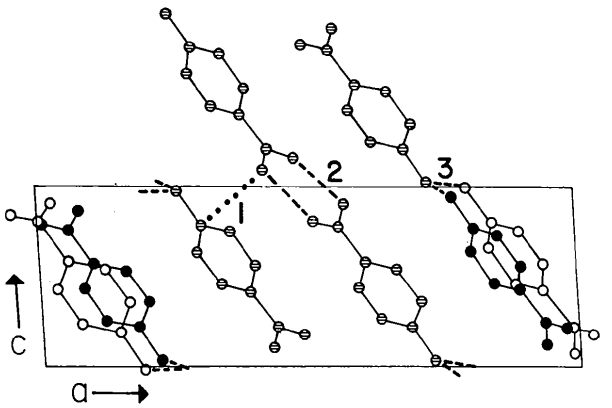

Fig. 3. Arrangement of molecules on the *ac* plane of the *p*-hydroxybenzoic acid crystal. The atoms shown by open circles are on the lowest level, those shown by circles with diagonal lines are on the intermediate level, and the filled circles designate atoms on the upper level. The shortest intermolecular distance of 3.288 Å is between C and O atoms (C5–O2) of adjacent molecules (distance 1, dotted line). The hydrogen bonds (2) between the two acid molecules (2.635 Å) are indicated by dashed lines. The hydrogen-bond distance (3) involving phenolic O atoms is 2.897 Å. The H atoms are not shown.

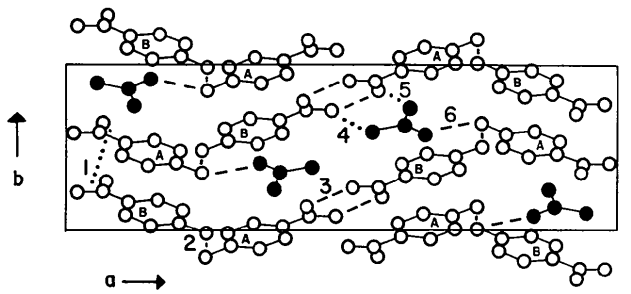

Fig. 4. Arrangement of molecules on the *ab* plane of *p*-hydroxybenzoic acid–acetone complex. Acetone molecules are shown with filled circles. The shortest intermolecular contact distance of 3.349 Å occurs between C atom *B*C1 and O atom *A*O2 of adjacent molecules (distance 1). The hydrogen-bond distance between phenolic O atoms is 2.761 Å (distance 2) and between dimerized carboxyl groups is 2.614 Å (distance 3). Acetone molecules are oriented so that C atom C10 and O atom *B*O1 are separated by 3.843 Å (distance 4), while C8 and *A*O2 are separated by 3.461 Å (distance 5). The hydrogen-bond distance between the phenolic O atoms and acetone O atoms is 2.675 Å (distance 6). H atoms are not shown.

The dimers in *p*-hydroxybenzoic acid are held together by hydrogen bonds (2.897 Å, Fig. 3) between phenolic groups; these hydrogen-bonded molecules spiral around the twofold screw axes to make up layers of dimers parallel to (401). In the acetone complex, a pair of dimers are linked through hydrogen-bonded phenolic O atoms (2.761 Å), and one of the phenolic O atoms is hydrogen bonded to the O atom in the acetone molecule (2.675 Å, Fig. 4); these hydrogen-bonded molecules of *p*-hydroxybenzoic acid and acetone spiral about the twofold screw axis. As a result, acetone molecules are situated in layers about adjacent chains of dimers, with the chains and layers running approximately parallel to (201).

In the pure acid and in molecules *A* and *B* of the complex, the benzene ring has essentially hexagonal symmetry, and the C atoms of the ring are practically coplanar within experimental error. In the pure acid, H atoms H1, H2 and H5, and O atom O2 deviate by the largest amounts [0.120 (6), 0.239 (6), 0.207 (6) and 0.149 (6) Å, respectively] from the plane of the benzene ring. In molecule *A* of the acetone complex, H atoms H1 and H5, and O atoms O1 and O2 deviate by the largest amounts [0.095 (4), −0.150 (4), 0.096 (4) and −0.114 (4) Å, respectively], while in molecule *B* of the acetone complex, H atom H1 and O atoms O1 and O2 deviate by the largest amounts [0.106 (3), −0.085 (3) and 0.128 (3) Å, respectively] from the plane of the benzene ring.

The structures of *p*-hydroxybenzoic acid and *p*-hydroxybenzoic acid–acetone complex reported here, as well as that previously reported for the monohydrate grown from wet acetone solution (*Beilsteins Handbuch der Organischen Chemie*, 1927; Fukuyama, Ohkura, Kashino & Haisa, 1973; Colapietro, Domenicano & Marciante, 1979), show that care must be exercised in growing uncomplexed crystals from solvents, especially when hydrogen-bonded complexes may be formed. *p*-Hydroxybenzoic acid monohydrate is obtained when crystals are grown in aqueous and in acetone solution, since even reagent-grade acetone contains some water [1% (Perrin, Armarego & Perrin, 1980)].

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Structure of the White-Line-Inducing Principle Isolated from *Pseudomonas Reactans*

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Abstract. $C_{54}H_{93}N_9O_{16}.H_2O$, $M_r = 1142.40$, orthorhombic, $P2_12_12_1$, $a = 14.230\ (1)$, $b = 24.370\ (5)$, $c = 18.780\ (2)$ Å, $V = 6512.6\ (11)$ Å^3, $Z = 4$, $D_x = 1.16$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.8$ cm^{-1}, $F(000) = 2472$, $T = 158\ (2)$ K, $R = 0.073$ for 6299 unique reflections. The structure of this cycle peptide is that of β-hydroxydecanoyl-L-Leu-D-Glu-D-*allo*-Thr-D-Val-D-Leu-D-Ser-D-Ser-L-Ile. Ring closure is through an ester linkage between the carboxyl of L-Ile and the hydroxyl of D-*allo*-Thr, leaving the γ-carboxyl of D-Glu free. The stereochemistry of the β-hydroxy acid is shown to be *R*.

Introduction. Members of the genus *Pseudomonas* characteristically produce a wide variety of extracellular compounds including siderophores, antibiotics, toxins and enzymes. A range of fluorescent *Pseudomonas* species are commonly found in association with the sporophore of the edible mushroom, *Agaricus bisporus* (Lange) Imbach (Olivier, Guillames & Martin, 1978; Zarkower, Wuest, Royse & Myers, 1983; Goor, Vantomme, Swings, Gillis, Kersters & deLey, 1986). Of particular interest is the taxonomically diverse group of saprophytic *Pseudomonas* species, collectively referred to as *Pseudomonas reactans* (Wong & Preece, 1979), which are capable of forming a white line in agar when grown in association with *Pseudomonas tolaasii* Paine, the causal organism of the economically significant brown blotch disease of *A. bisporus* (Tolaas, 1915). This white-line reaction is a rapid and reliable means of identifying *P. tolaasii* isolates (Zarkower, Wuest, Royse & Myers, 1983; Wong & Preece, 1979) and is the result of a specific interaction between a diffusible peptide (Mortishire-Smith, Nutkins, Packman, Brodey, Rainey, Johnstone & Williams, 1991) produced by *P. reactans* (called the 'white-line-inducing principle' or WLIP) and the water-soluble peptide toxin (tolaasin) produced by *P. tolaasii* (Peng, 1986; Nutkins, Mortishire-Smith, Packman, Brodey, Rainey, Johnstone & Williams, 1991; Mortishire-Smith, Drake, Nutkins & Williams, 1991). Neither the mechanism whereby the two peptides give rise to

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