bzw. 0,187 Å. Es ist also kein Zusammenhang zwischen dem Abstand des N-Atoms von seiner Ligandenebene und dem N—Carbonylabstand im β-Lactamring zu erkennen.

Zumindest in den hier diskutierten Fällen trifft die These (van Heyningen & Ahern, 1968) nicht zu, dass der N—Carbonylabstand in Cephemen mit dem Abstand des Stickstoffatoms von seiner Ligandenebene zunimmt und damit auch die Reaktivität dieser Bindung. Aufgrund dieser These hatte man gefolgert, dass zwar Δ3-Cepheme eine antibiotische Wirksamkeit gegen die Synthese von Bakterienzellwänden entfalten können, aber nicht die Δ2-Cepheme (Sweet & Dahl, 1970).

Im Kristall werden schwache Wasserstoffbrückenbindungen (2,969 Å) zwischen dem Stickstoffatom der Phenylacetaminogruppe und dem Lactamsauerstoffatom von zwei verschiedenen Molekülen ausgebildet (Fig. 2).

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4′,6,7-Trihydroxyflavylium Chloride Monohydrate; a Synthetic Anthocyanidin

By Kathuhiko Ueno

Research Institute for Polymers and Textiles, Sawatari 4, *Kanagawa-ku, Yokohama* 221, *Japan*

and Norio Saito

Chemical Laboratory, Meiji-gakuin University, Minato-ku, Tokyo 108, *Japan*

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Abstract. $C_{15}H_{11}O_4.Cl.H_2O$, orthorhombic, $Pca2_1$, $a = 29{\cdot}819$ (5), $b = 6{\cdot}196$ (1), $c = 7{\cdot}634$ (1) Å, $U = 1410{\cdot}5$ (3) Å^3 with $Z = 4$, $D_m = 1{\cdot}456$, $D_x = 1{\cdot}463$ g cm^{-3}, F.W. 308·7, $R = 0{\cdot}042$ for 1266 observed reflexions. The benzopyrylium portion of the molecule is approximately planar, and the phenyl ring makes an angle of 5·9° with this plane.

Introduction. Anthocyanidins are a group of glycosidic pigments responsible for various shades of colour from blue to pink in plants. The common constituent of all anthocyanins and anthocyanidins was established by Willstätter and later by Robinson (Bentley, 1962) to be the 2-phenylbenzopyrylium or flavylium cation. The colour of these substances is sensitive to hydroxyl, methoxyl and glycosidyl substitution. More dramatic colour variations *in vivo* take place with co-pigmentation, metal complexing and *p*H changes (Hayashi, 1962; Harborne, 1965). To understand these it is necessary to determine the anthocyanidin structures in detail.

The sample was synthesized by Hayashi (1933). Single crystals were prepared by slow evaporation from ethanolic hydrochloric acid. They were orange plates elongated along the *b* axis. The space groups $Pca2_1$ and *Pcam* were indicated by the systematic absences on Weissenberg photographs of *h*0*l* and 0*kl* reflexions with *h* and *l* odd respectively. The density was measured by flotation in a mixture of *n*-hexane and carbon tetrachloride.

Measurements of lattice constants and intensities up to 153° in 2θ were made on a Rigaku four-circle diffractometer using Cu $K\alpha$ radiation monochromatized by graphite. A crystal of dimensions 0·05 × 0·2 × 0·1 mm was used. The $2\theta/\omega$ scan technique was applied with a scan rate of $2°(2\theta)$ min^{-1}. Background counts were made for 20 s at the beginning and end of each scan. The reflexions with $|F_o|$ less than $20\sigma(|F_o|)$ were measured up to three times and the accumulated counts were used. Out of 1441 independent reflexions measured, 1226 had $|F_o|$ values larger than $3\sigma(|F_o|)$. No correction was made for absorption ($\mu = 26{\cdot}8$ cm^{-1}).

Table 1. *Fractional atomic coordinates and thermal parameters with their estimated standard deviations in parentheses*

The anisotropic temperature factor has the form: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$, and their β_{ij} values are multiplied by 10^4.

	$x(\times 10^5)$	$y(\times 10^4)$	$z(\times 10^4)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	37097 (3)	6665 (2)	4716 (2)	8·4 (1)	249 (3)	208 (2)	−4 (1)	7 (1)	1 (7)
O(1)	12079 (8)	5284 (4)	4011 (4)	6·2 (3)	171 (8)	163 (7)	−1 (3)	3 (3)	−52 (13)
C(2)	11511 (13)	3429 (6)	3132 (6)	8·2 (5)	153 (11)	153 (10)	2 (4)	−4 (4)	2 (21)
C(3)	15248 (13)	2305 (7)	2579 (7)	8·3 (5)	167 (11)	163 (10)	6 (4)	2 (4)	−15 (20)
C(4)	19497 (13)	3069 (7)	2896 (7)	7·9 (5)	171 (12)	170 (10)	15 (4)	4 (4)	−2 (21)
C(5)	24286 (13)	5908 (6)	4255 (6)	6·8 (5)	191 (10)	179 (12)	4 (4)	10 (4)	12 (19)
C(6)	24522 (14)	7822 (6)	5187 (6)	6·8 (5)	214 (11)	166 (11)	−4 (4)	4 (4)	69 (20)
C(7)	20453 (13)	8870 (7)	5694 (6)	9·4 (5)	171 (12)	148 (9)	−6 (4)	−4 (4)	39 (20)
C(8)	16307 (13)	8019 (7)	5288 (6)	7·7 (5)	170 (11)	159 (11)	−2 (4)	9 (4)	−2 (20)
C(9)	16234 (12)	6091 (6)	4346 (6)	6·5 (4)	166 (11)	182 (12)	−5 (4)	−3 (4)	47 (20)
C(10)	20083 (12)	4989 (7)	3833 (7)	7·0 (4)	177 (11)	146 (9)	4 (4)	5 (4)	28 (21)
C(1′)	6822 (13)	2829 (7)	2965 (8)	8·0 (5)	177 (12)	154 (10)	−1 (4)	7 (4)	−8 (20)
C(2′)	3395 (13)	4198 (7)	3524 (7)	8·3 (5)	192 (12)	223 (12)	−3 (4)	0 (5)	−50 (23)
C(3′)	−1014 (13)	3596 (7)	3395 (7)	7·3 (5)	206 (13)	237 (12)	−1 (4)	6 (4)	−62 (24)
C(4′)	−2115 (14)	1603 (7)	2659 (7)	8·2 (5)	257 (14)	182 (10)	−13 (5)	−3 (4)	−59 (26)
C(5′)	1218 (13)	241 (8)	2077 (7)	8·8 (6)	278 (16)	232 (13)	−14 (5)	15 (5)	−186 (27)
C(6′)	5646 (14)	836 (8)	2212 (7)	9·2 (5)	239 (14)	259 (15)	1 (5)	11 (5)	−168 (27)
O(6)	28328 (9)	8830 (5)	5635 (5)	7·6 (3)	250 (9)	222 (8)	−11 (3)	4 (3)	−59 (16)
O(7)	20961 (9)	10713 (5)	6623 (5)	8·8 (3)	213 (9)	215 (7)	−4 (3)	−3 (3)	−146 (15)
O(4′)	−6434 (9)	908 (5)	2545 (5)	7·4 (3)	346 (11)	323 (10)	−19 (4)	0 (3)	−230 (22)
O(*W*)	36815 (11)	2491 (5)	2431 (6)	12·3 (4)	268 (10)	349 (11)	6 (4)	−27 (4)	−181 (20)

	$x(\times 10^4)$	$y(\times 10^3)$	$z(\times 10^3)$	B(Å^2)		$x(\times 10^4)$	$y(\times 10^3)$	$z(\times 10^3)$	B(Å^2)
H(C3)	1468 (13)	94 (7)	196 (6)	2·1 (10)	H(C3′)	−371 (13)	459 (7)	386 (7)	3·0 (11)
H(C4)	2222 (12)	216 (6)	239 (6)	1·5 (10)	H(O4′)	−799 (15)	188 (8)	313 (7)	3·8 (13)
H(C5)	2729 (12)	511 (7)	395 (6)	2·7 (11)	H(C5′)	30 (18)	−128 (7)	136 (8)	4·6 (14)
H(O6)	3108 (14)	801 (8)	519 (7)	4·0 (13)	H(C6′)	828 (15)	−20 (8)	212 (7)	4·4 (14)
H(O7)	1807 (16)	1129 (8)	687 (7)	4·8 (14)	H(*WA*)	3696 (17)	353 (8)	315 (7)	5·3 (15)
H(C8)	1312 (12)	872 (6)	548 (5)	1·3 (10)	H(*WB*)	3977 (17)	184 (8)	260 (6)	6·0 (16)
H(C2′)	470 (14)	559 (7)	418 (6)	3·4 (12)					

The space group *Pcam* was rejected because it would require the molecule to lie in a mirror plane, and a three-dimensional Patterson function showed no such feature. The structure was solved by the direct method (Karle & Karle, 1966). Starting with four phases defining the origin and enantiomer, and with two symbols, the tangent formula (Karle & Hauptman, 1956) was used to evaluate the phases of 160 reflexions with $|E| \geq 1{\cdot}45$. The phase set with the lowest *R* value (Karle & Karle, 1966) gave an *E* map which revealed the Cl, fifteen C and two O atoms. All other non-hydrogen atoms emerged on successive Fourier syntheses. When *R* reached 0·07 by block-diagonal-matrix least-squares refinement all the H atoms were located on a difference map. The final *R* was 0·042 for all the observed reflexions.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Table 1 shows the atomic coordinates and thermal parameters with their estimated standard deviations.

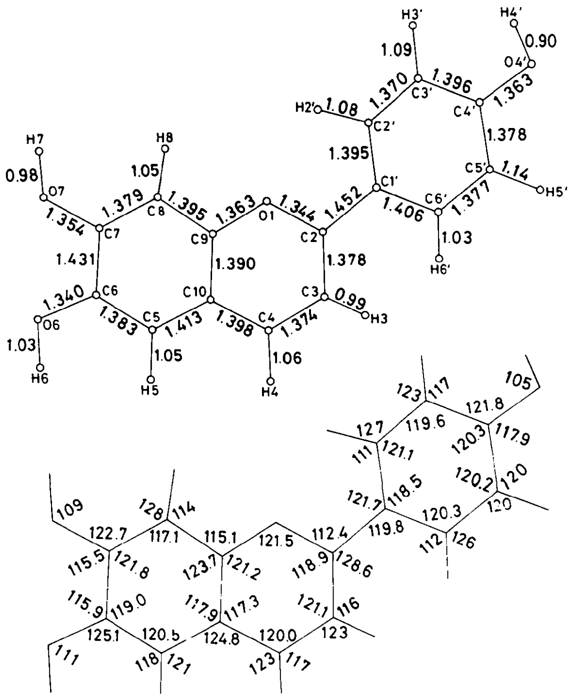

Fig. 1. Bond lengths and angles. The estimated standard deviations for distances and angles involving heavy atoms are 0·006–0·007 Å and 0·4–0·5°, and those involving H atoms are 0·04–0·05 Å and 2–3°.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31960 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

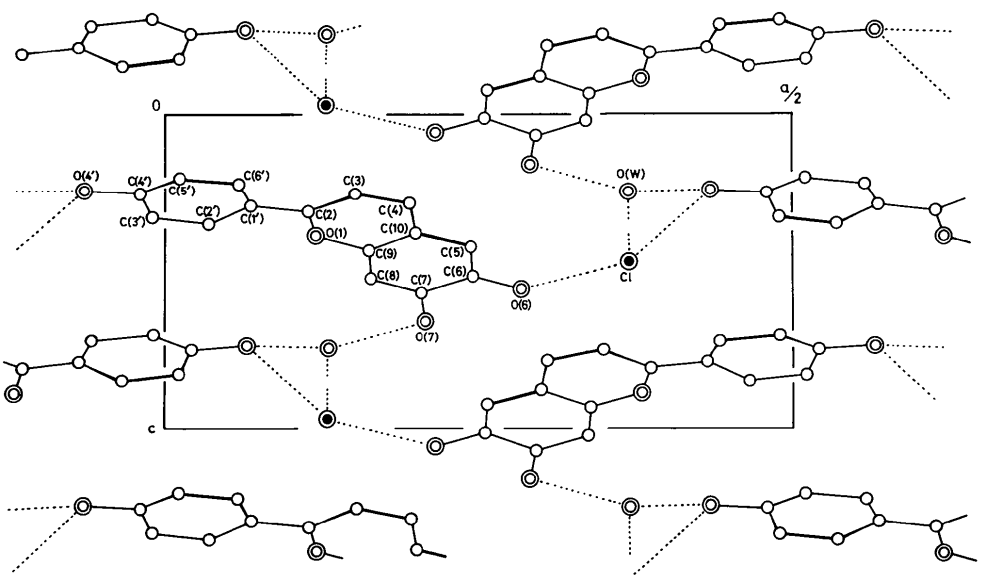

Fig. 2. Crystal structure projected along the *b* axis. The hydrogen bonds are indicated by broken lines.

Table 2. *Hydrogen bonds and short intermolecular distances less than* 3·2 Å (*where the* Cl *atom is involved the limit is* 3·4 Å)

Hydrogen bonds

Donor atom	Acceptor atom	Distances (Å) $D\cdots A$	Distances (Å) $\mathrm{H}\cdots A$	Angle (°) O—H···O (or Cl)
O(4′)	$\cdots\mathrm{Cl}^{\mathrm{ii}}$	2·954	2·10	162
O(6)	$\cdots\mathrm{Cl}^{\mathrm{i}}$	3·021	2·01	169
O(*W*)	$\cdots\mathrm{Cl}^{\mathrm{i}}$	3·121	2·28	171
O(*W*)	$\cdots\mathrm{O(4')}^{\mathrm{iii}}$	2·915	2·05	147
O(7)	$\cdots\mathrm{O}(W)^{\mathrm{iv}}$	2·640	1·69	175

Other short intermolecular distances

$\mathrm{O(1)}\cdots\mathrm{O}(2W)^{\mathrm{v}}$	3·150	$\mathrm{O(1)}\cdots\mathrm{Cl}^{\mathrm{vii}}$	3·400
$\mathrm{C(4)}\cdots\mathrm{O(6)}^{\mathrm{vi}}$	3·209	$\mathrm{C(2)}\cdots\mathrm{Cl}^{\mathrm{vii}}$	3·316

Symmetry code

(i) x, y, z

(ii) $-\frac{1}{2}+x, 1-y, z$

(iii) $\frac{1}{2}+x, -y, z$

(iv) $\frac{1}{2}-x, 1+y, \frac{1}{2}+z$

(v) $\frac{1}{2}-x, y, \frac{1}{2}+z$

(vi) $\frac{1}{2}-x, -1+y, -\frac{1}{2}+z$

(vii) $\frac{1}{2}-x, y, -\frac{1}{2}+z$

Discussion. The bond lengths and angles are shown in Fig. 1. The mean estimated standard deviations are 0·006 Å and 0·4°. The benzopyrylium portion and the phenyl ring are both planar and the angle between the planes is 5·9°. This value is close to that of apigeninidin (4·1°, Busetta, Colleter & Gadret, 1974). In the heterocyclic ring the C(9)—O(1) bond length is nearly equal to the C—O bond distance of furan (1·368 Å, Fourme, 1969), but the O(1)—C(2) length is shorter. In the benzopyrylium portion, C(6)—C(7) and C(8)—C(9) are longer than the corresponding bonds in apigeninidin (1·41 and 1·36 Å), whereas C(7)—C(8) and C(9)—C(10) are shorter (1·40 and 1·41 Å).

C(2)—C(1′) is shorter than the single-bond length. This indicates that the π electrons are delocalized throughout the anthocyanidin molecule. The C(3)—C(2)—C(1′) bond angle is larger than O(1)—C(2)—C(1′), probably because of repulsion between H(3) and H(6′) (2·04 Å).

As is shown in Fig. 2, the cation molecule, chloride ion and water molecule are linked by hydrogen bonds, whose geometries are given in Table 2. The water molecule forms three hydrogen bonds in an approximately planar trigonal arrangement. The ring oxygen is not an acceptor of any hydrogen bond. The shortest intermolecular distance between the anthocyanidin molecule and chloride ion, other than a hydrogen bond, involves C(2).

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