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Cyanidin Bromide Monohydrate (3,5,7,3′,4′-Pentahydroxyflavylium Bromide Monohydrate)

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Abstract. $C_{15}H_{11}O_6.Br.H_2O$, monoclinic, $P2_1/n$ (No. 14), $a = 4{\cdot}808$ (1), $b = 16{\cdot}461$ (3), $c = 18{\cdot}750$ (3) Å, $\beta = 96{\cdot}07$ (1)°, $U = 1475{\cdot}3$ (3) Å^3, F.W. 385·2, $Z = 4$, $D_m = 1{\cdot}74$, $D_x = 1{\cdot}73$ g cm^{-3}, $R = 0{\cdot}040$ for 2240 observed reflexions. The benzopyrylium portion of the molecule is approximately planar and the phenyl ring makes an angle of 10·1° with this plane. The bromide ion is hydrogen bonded to the 3′- and 7-hydroxyl groups of the cyanidin molecule, and to the water molecules. The hydroxyl groups O(3)H and O(4′)H are hydrogen bonded to the water molecule, and O(5)H forms a bifurcated hydrogen bond with O(3′) and O(4′).

Introduction. Cyanidin, one of the 3-hydroxyanthocyanidins, is a common plant pigment. The crystal structures of two 3-deoxyanthocyanidins have already been reported and these molecules have been shown to have almost planar structures (Busetta, Colleter & Gadret, 1974; Ueno & Saito, 1977). Their spectral features are different from those of the present compound (Harborne, 1968). The present investigation was

Table 1. *Fractional atomic coordinates and thermal parameters*

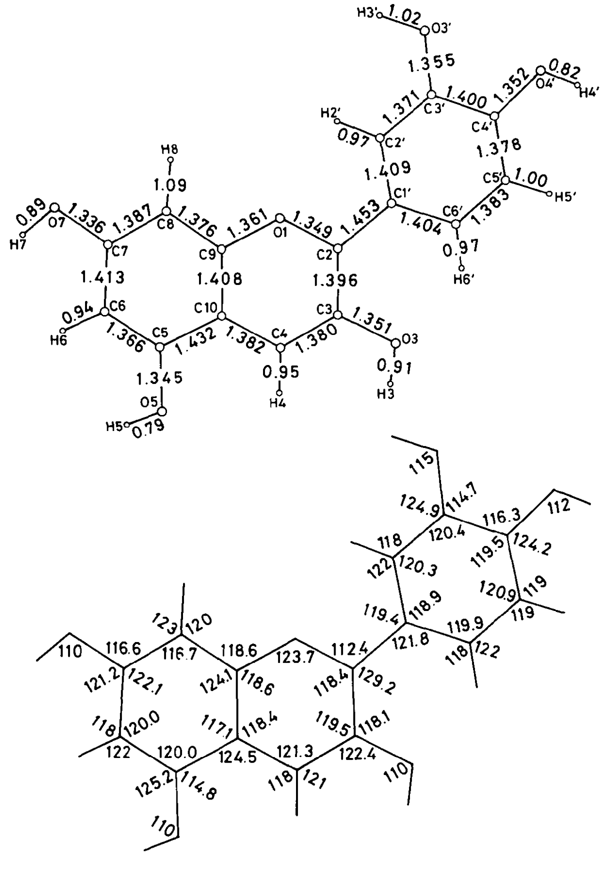
The anisotropic temperature factor has the form: $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$. Estimated standard deviations are in parentheses.

	x ($\times 10^4$)	y ($\times 10^5$)	z ($\times 10^5$)	β_{11} ($\times 10^4$)	β_{22} ($\times 10^5$)	β_{33} ($\times 10^5$)	β_{12} ($\times 10^4$)	β_{13} ($\times 10^4$)	β_{23} ($\times 10^5$)
Br	3447 (1)	4597 (3)	17545 (3)	457 (2)	347 (2)	343 (1)	59 (1)	104 (1)	16 (3)
O(1)	1710 (5)	26492 (14)	49845 (12)	240 (11)	213 (9)	142 (7)	−24 (5)	62 (4)	−31 (13)
C(2)	325 (7)	19401 (20)	48720 (18)	236 (17)	174 (13)	149 (10)	−6 (7)	32 (6)	28 (18)
C(3)	731 (7)	14923 (21)	42591 (18)	294 (18)	204 (14)	160 (11)	−25 (8)	54 (7)	−26 (19)
C(4)	2591 (8)	17696 (21)	38024 (18)	319 (18)	216 (14)	134 (10)	−2 (8)	58 (7)	−33 (19)
C(5)	6010 (7)	28132 (22)	34880 (18)	254 (17)	275 (15)	121 (10)	−15 (8)	39 (7)	17 (20)
C(6)	7278 (7)	35414 (23)	36552 (18)	243 (17)	268 (15)	160 (11)	−37 (8)	45 (7)	63 (20)
C(7)	6619 (7)	39798 (22)	42629 (19)	247 (17)	233 (15)	189 (11)	−36 (8)	14 (7)	11 (20)
C(8)	4740 (8)	36889 (22)	47143 (18)	274 (17)	237 (14)	163 (11)	−14 (8)	34 (7)	−52 (20)
C(9)	3497 (7)	29531 (21)	45350 (17)	233 (16)	221 (14)	126 (10)	−13 (8)	31 (6)	57 (19)
C(10)	4018 (7)	24929 (21)	39303 (17)	216 (16)	211 (13)	131 (10)	−6 (7)	30 (6)	17 (18)
C(1′)	−1469 (7)	17641 (21)	54292 (17)	229 (16)	222 (14)	124 (10)	−8 (7)	44 (6)	11 (19)
C(2′)	−1948 (7)	23718 (22)	59314 (18)	261 (17)	230 (14)	136 (10)	−10 (8)	39 (7)	−22 (19)
C(3′)	−3709 (7)	22280 (22)	64467 (18)	265 (17)	248 (15)	143 (10)	0 (8)	51 (7)	−63 (20)
C(4′)	−5013 (7)	14713 (22)	64883 (18)	254 (17)	263 (17)	145 (10)	8 (8)	57 (7)	34 (20)
C(5′)	−4481 (8)	8657 (23)	60141 (19)	422 (21)	223 (15)	186 (12)	−31 (9)	90 (8)	−10 (21)
C(6′)	−2769 (8)	10057 (22)	54784 (19)	410 (21)	208 (14)	188 (11)	−12 (9)	97 (8)	−38 (21)
O(3)	−745 (6)	7990 (16)	41350 (14)	539 (16)	267 (11)	213 (8)	−121 (7)	131 (6)	−163 (16)
O(5)	6512 (6)	23368 (17)	29329 (13)	441 (15)	337 (12)	178 (8)	−90 (7)	117 (6)	−115 (16)
O(7)	7860 (6)	46871 (16)	44438 (14)	397 (14)	282 (12)	270 (9)	−99 (7)	171 (6)	−116 (17)
O(3′)	−4375 (7)	27781 (18)	69384 (16)	626 (19)	322 (13)	337 (11)	−85 (8)	187 (7)	−219 (19)
O(4′)	−6730 (6)	13867 (16)	70096 (13)	438 (14)	273 (11)	190 (8)	−52 (7)	120 (6)	−36 (15)
O(*W*)	8877 (6)	1289 (17)	28529 (14)	401 (14)	377 (13)	201 (9)	−46 (7)	74 (6)	−44 (17)

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B (Å^2)		x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B (Å^2)
H(O3)	−75 (9)	65 (3)	367 (2)	2·3 (10)	H(O3′)	−355 (10)	335 (4)	689 (3)	5·8 (13)
H(C4)	299 (9)	145 (3)	340 (2)	1·9 (10)	H(O4′)	−743 (10)	94 (3)	701 (2)	3·6 (12)
H(O5)	736 (10)	258 (3)	267 (2)	2·9 (11)	H(C5′)	−521 (7)	30 (2)	608 (2)	0·5 (8)
H(C6)	856 (8)	377 (2)	337 (2)	1·3 (9)	H(C6′)	−236 (8)	59 (2)	514 (2)	1·4 (9)
H(O7)	892 (10)	484 (3)	411 (3)	3·6 (12)	H(*WA*)	1008 (9)	17 (3)	263 (2)	2·8 (11)
H(C8)	439 (9)	398 (3)	522 (2)	2·0 (10)	H(*WB*)	770 (10)	34 (3)	260 (3)	4·0 (12)
H(C2′)	−105 (9)	290 (3)	593 (2)	2·4 (10)					

undertaken to examine the steric effect of the 3-hydroxyl group on the conformation of anthocyanidin.

Dark-red needle crystals were prepared from methanolic hydrobromic acid. Preliminary X-ray photographs showed that the crystals are monoclinic, space group $P2_1/n$ from the systematic absences $h0l$ for $h + l$ odd and $0k0$ for k odd. The unit-cell dimensions were obtained from the least-squares refinement of the 2θ values of 25 reflexions obtained on a Rigaku four-circle diffractometer. Intensity data up to 153° in 2θ with Cu $K\alpha$ radiation monochromatized with graphite were collected on the diffractometer. A crystal of dimensions $0{\cdot}1 \times 0{\cdot}08 \times 0{\cdot}05$ mm was used. The $2\theta/\omega$ scan was employed with a scan rate of 2° (2θ) min^{-1}. The scan range was $(1{\cdot}0 + 0{\cdot}5 \tan\theta)°$, and the backgrounds were measured 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. Of 2915 independent reflexions measured, 2240 were greater than $3\sigma(|F_o|)$. No correction was made for absorption ($\mu = 44{\cdot}1$ cm^{-1}).



ig. 1. Bond lengths and angles. The estimated standard deviations for distances and angles involving heavy atoms are 0·004–0·005 Å and 0·3–0·4°, and those involving H atoms are 0·04–0·05 Å and 2–4°.

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966), using 330 reflexions with $|E| \geq 1{\cdot}60$. Block-diagonal least-squares refinement gave an R value of 0·057. A difference Fourier synthesis at this stage revealed all the H atoms. In the subsequent refinement the positional and thermal parameters for the H atoms were allowed to vary. The final R was 0·040 for 2240 observed reflexions.* The weighting scheme was $w = |F_o|/10{\cdot}0$ if $|F_o| < 10{\cdot}0$, $w = 1{\cdot}0$ if $10{\cdot}0 \leq |F_o| < 50{\cdot}0$ and $w = 50{\cdot}0/|F_o|$ if $|F_o| \geq 50{\cdot}0$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and thermal parameters are given in Table 1.

Discussion. The bond lengths and angles are shown in Fig. 1. The benzopyrylium portion and the phenyl ring are both planar within experimental error. The angle between the planes is 10·1°, which is somewhat larger than the values 5·9° in the 4′,6,7-trihydroxyflavylium cation (Ueno & Saito, 1977) and 4·1° in apigeninidin (Busetta *et al.*, 1974), probably because of the repulsion between O(3) and H(6′) (2·14 Å). The C(2)–C(1′) bond length is close to the values in these two anthocyanidins. In the benzopyrylium portion the bond lengths are close to the corresponding lengths in apigeninidin. The C(3)–C(2)–(1′) bond angle is comparable to the value of 128·6° in the 4′,6,7-trihydroxyflavylium cation.

Table 2. *Hydrogen bonds and short intermolecular distances less than* 3·4 Å

Hydrogen bonds

Donor atom		Acceptor atom	Distances (Å) $D\cdots A$	$H\cdots A$	Angle (°) O–H···O (or Cl)
O(7)	···	Br^{v}	3·265	2·39	172
O(3′)	···	Br^{vi}	3·236	2·21	177
O(W)	···	Br^{ii}	3·213	2·46	170
O(W)	···	Br^{i}	3·196	2·46	158
O(3)	···	O(W)^{iii}	2·634	1·75	165
O(5)	···	O(3′)^{vii}	2·864	2·27	133
O(5)	···	O(4′)^{vii}	2·905	2·17	156
O(4′)	···	O(W)^{iv}	2·722	1·91	172

Other short intermolecular distances

C(6)	···	O(4′)^{vii}	3·174
O(5)	···	O(3′)^{viii}	3·226

Symmetry code

(i) x, y, z	(ii) $1 + x, y, z$
(iii) $-1 + x, y, z$	(iv) $-x, -y, 1 - z$
(v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(vi) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
(vii) $\frac{3}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$	(viii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31961 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The crystal structure projected along the *a* axis is shown in Fig. 2. The hydrogen bonds are given in Table 2, together with short intermolecular contacts less than 3·3 Å. The cyanidin molecule is hydrogen bonded to bromide ions through O(7)H and O(3′)H, and also to water molecules through O(3)H and O(4′)H. The O(5)H group forms a bifurcated hydrogen bond with O(3′) and O(4′).

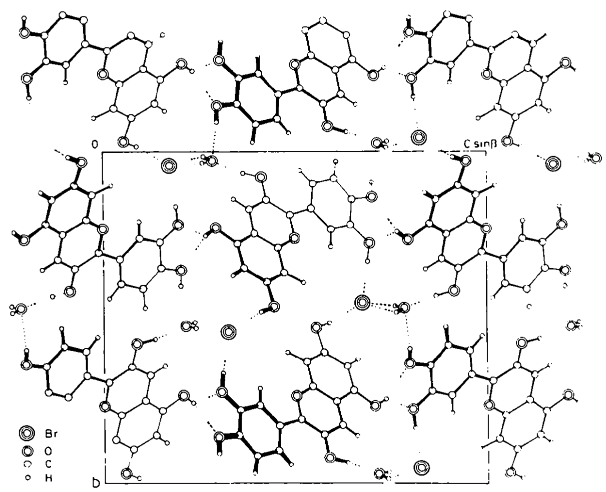

Fig. 2. Crystal structure projected along the *a* axis. The hydrogen bonds are indicated by broken lines.

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Benzyloxycarbonylglycyl-L-proline

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Abstract. $C_{15}H_{18}N_2O_5$, tetragonal, $P4_32_12$; $a = 9{\cdot}455$ (1), $c = 34{\cdot}889$ (5) Å; $Z = 8$, $D_x = 1{\cdot}305$, $D_m = 1{\cdot}288$ g cm^{-3}. The structure was solved by the direct method and refined to a final R value of 0·051. The molecules are in an antiparallel arrangement and are connected by hydrogen bonds.

Introduction. A series of oligopeptides containing Gly-Pro sequences, such as (*o*-Br)-*Z*-Gly-Pro-Leu-Gly-Pro (Ueki, Bando, Ashida & Kakudo, 1971), *Z*-Gly-Pro-Leu-Gly-Pro (Bando, Tanaka, Ashida & Kakudo, 1976), (*p*-Br)-*Z*-Gly-Pro-Leu-Gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969) and *Z*-Gly-Pro-Leu (Yamane, Ashida, Shimonishi, Kakudo & Sasada, 1976) have been studied by X-ray diffraction. It was revealed that the tetra- and pentapeptides have essentially the same conformation, *i.e.* β-turn. On the other hand, the structure of the tripeptide was found to be different from those of the tetra- and pentapeptides, and was shown to have a *cis* conformation at the peptide bond between Gly and Pro.

The present paper describes the crystal structure of $C_{15}H_{18}N_2O_5$ (*Z*-Gly-Pro), and the conformation is compared with those of the longer peptides.

The X-ray diffraction data were collected on a Rigaku four-circle automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation, the θ–2θ scan, and a scan rate of 4° (2θ) min^{-1}. 1445 independent reflexions with $\sin\theta/\lambda$ less than 0·562 were measured. The structure was solved by *MULTAN* (Germain, Main & Woolfson,