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THE CRYSTAL AND MOLECULAR STRUCTURE OF PELARGONIDIN BROMIDE MONOHYDRATE*

Norio Saito
Chemical Laboratory, Meiji-gakuin University, Totsuka-ku,
Yokohama 221, Japan
Katsuhiko Ueno
Research Institute for Polymers and Textiles, Yatabe-Higashi
1-1-4, Tsukuba, Ibaraki 305, Japan

Abstract——The structure of pelargonidin, 3,5,7,4'-tetrahydroxyflavylium, bromide monohydrate, obtained by the hydrolysis of pelargonin, the major pigment of Dahlia variabilis has been determined by the X-ray method. The crystals are triclinic space group $P\bar{1}$ with a=8.929(2), b=11.360(3), c=7.299(2)Å, α=95.00(5), β=93.61(5), γ=93.35(5)° and Z=2. The structure was solved by the heavy atom method and refined by least-squares to a final R-value of 0.057 for 2351 observed reflexions. The molecule is nearly planar. The phenyl ring makes a dihedral angle of only 3.8° with the benzopyrylium plane. The sp^2-sp^2 single bond connecting the benzopyrylium portion and phenyl ring is 1.458Å. The bond lengths in the benzopyrylium portion show a charasteristic feature of resonance structure. The hydroxyl groups at the 7- and 4'-positions of pelargonidin cation form hydrogen bond with Br ions. The pelargonidin molecules related by the center of symmetries are stacked along the c axis. The hydrogen bonding schemes and stacking modes of anthocyanidins so far determined are summarized.

During the course of investigations on the flower colour variation due to pH change, self-association and copigmentation of anthocyanin pigments[1] in vivo[2], it become necessory to know the detail information of the molecular structures and interaction

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* Dedicated to Dr. Kozo Hayashi, on the occasion of his 77th birthday.

between anthocyanins molecules. Till now three structures of anthocyanidin salts have been published. They are two 3-deoxyanthocyanidins[3-4], and one 3-hydroxyanthocyanidin[5]. All of them show almost planar conformations and strong contribution of 7- and 4'-hydroxyl groups on the resonance structure. This paper deals with the X-ray structure determination of pelargonidin bromide monohydrate(I), one of the most widely spreaded naturally occurring 3-hydroxyanthocyanidins, in order to give a clue to the chemical basis of the colour variation due to anthocyanins.

The flavylium moiety is nearly planar. The maximum deviation from the mean plane is 0.025Å. The dihedral angle between flavylium moiety and the phenyl ring B is only 3.8°. Thus, the molecule can be expressed to be nearly planar as a whole.

The bond lengths and angles with the numbering system used are shown in Fig.1.

The C2-C1' bond length, 1.458Å, is considerably shorter than the sp^2-sp^2 single bond such as in biphenyl(1.497Å) or butadiene(1.48Å). These values are comparable to the other anthocyanidin salts such as in cyanidin·Br·H_2O(II)[5], 6,7,4'-trihydroxyflavylium·Cl·H_2O(III)[4] and apigeninidin·Cl·H_2O(IV)[3](Table in Fig.2).

The mean value of C-C bond length in the ring A is 1.398Å. The C5-C6, C8-C9 and C6-C7 bonds are rather short and C5-C10 is considerably longer than the mean value. This feature of bond lengths is close to the benzene portion of coumarin derivatives[6]. In the ring C, C4-C10 bond length is somewhat shorter than C2-C3 and C3-C4 bonds. The O1-C2 bond length is shorter than O1-C9 by 0.035Å. These tendencies are close to the other anthocyanidins so far determined. The hydroxyl C-OH bond lengths are in the range from 1.336 to 1.368Å.

The bond angle C3-C2-C1' is larger than O1-C2-C1' by 15.8° probably owing to the repulsion between O3 and H6'(2.22Å). Close values of difference in corresponding bond angles are observed in (II), (III) and (IV), 16.8°, 16.2° and 11.9°, respectively. The C8-C9-C10 is larger than the usual sp^2 bond angle(120°). On the other hand, C9-C10-C5, O1-C9-C10 and C7-C8-C9 are rather small. This feature is commonly observed in (II), (II) and (IV).

Some possible limitting structures are shown in Fig.3. The shortening in the C2-C1' length together with the planarity of the molecule indicates the dominance of the structure(2). A strong contribution from the structures(3) is also indicated on the basis of the consideration of the bond lengths in the rings A and C. Anthocyanidin cation is usually designated as structure(1) which is accessible from the observation of the difference in bond lengths between O1-C2 and O1-C9, though the contribution may be less. A little contribution of hydroxyl group O5H(structure(4))

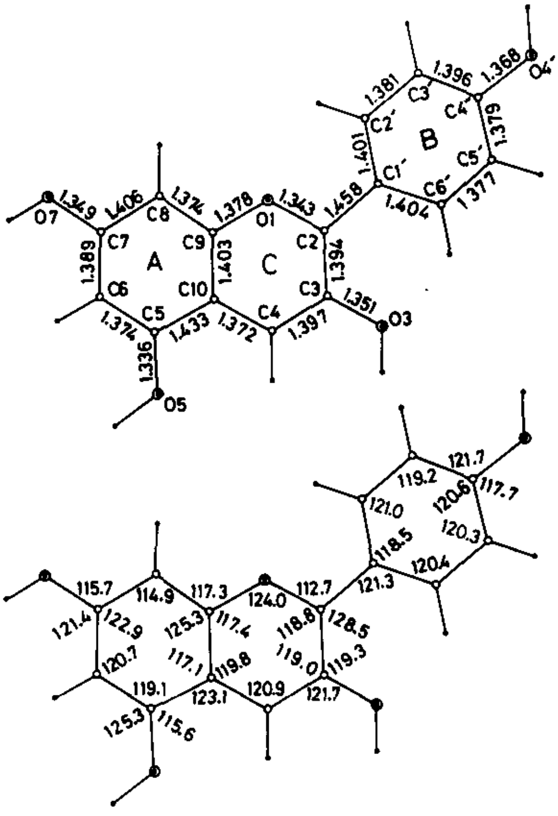


Fig.1. Bond lengths(Å) and angles(°) The estimated standard deviations are 0.005-0.006Å for lengths and 0.3-0.4° for angles.

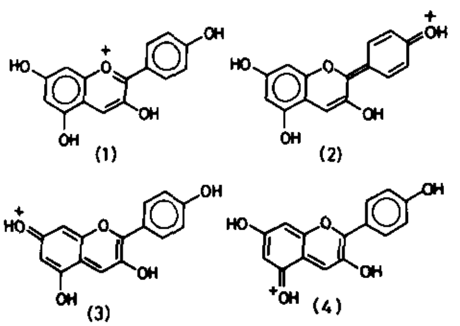


Fig.3. Possible limitted structures.

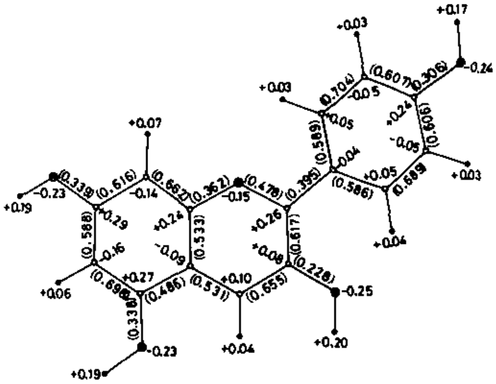
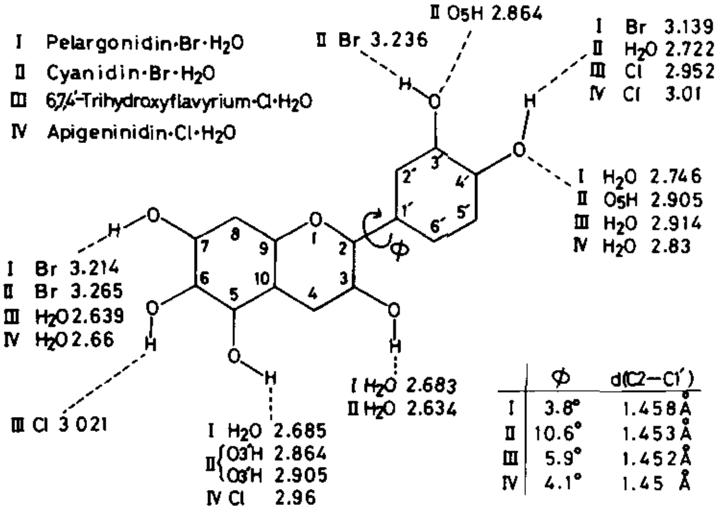


Fig.4. Net charge densities and π-bond orders in parentheses calculated by CNDO/2 method.



	Φ	d(C2−C1')
I	3.6°	1.458Å
II	10.6°	1.453Å
III	5.9°	1.452Å
IV	4.1°	1.45 Å

Fig.2. Hydrogen bonding schemes and lengths(Å). The table shows the conformations around the C2-C1' bonds.

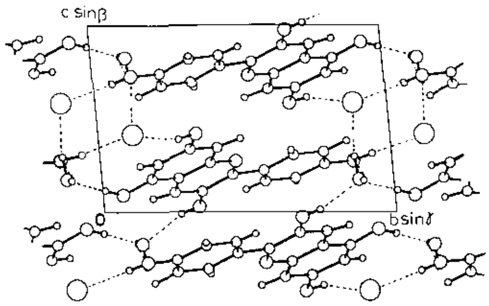


Fig.5. Crystal structure viewed along the a axis. Hydrogen bonds are indicated by broken lines.

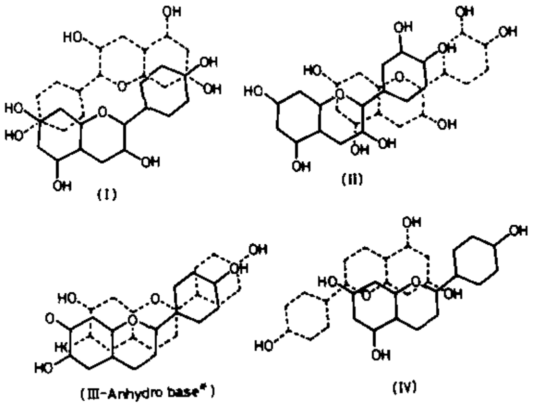


Fig. 6. Stacking modes of anthocyanidin planes. *Anhydrobase of (III)(Ref.7).

Table 1. Final atomic parameters. The atomic coordinates and anisotropic thermal parameters are multiplied by 10^5(Br atom) or 10^4(C, O atoms). The anisotropic coefficients have a form $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	27638(6)	11868(4)	41577(8)	1064(5)	580(3)	2882(13)	159(6)	-251(13)	-78(9)
O1	5826(3)	4640(2)	2700(4)	69(3)	35(2)	149(6)	30(4)	-40(7)	-21(5)
C2	4398(4)	4497(3)	1978(5)	65(5)	38(3)	147(10)	34(6)	-19(4)	-14(8)
C3	3881(4)	3398(3)	1090(6)	65(5)	41(3)	164(11)	15(6)	-31(11)	-7(9)
C4	4849(4)	2474(3)	1031(6)	87(5)	29(3)	170(10)	11(6)	-11(12)	-4(8)
C5	7336(4)	1725(3)	1770(6)	84(5)	28(3)	177(11)	32(6)	-38(12)	-28(8)
C6	8769(4)	1976(3)	2566(6)	79(5)	39(3)	178(10)	96(6)	-53(12)	-11(9)
C7	9219(4)	3107(3)	3361(6)	74(5)	41(3)	179(11)	21(6)	-30(12)	19(9)
C8	8252(4)	4042(3)	3435(6)	84(5)	40(3)	147(10)	7(6)	-35(12)	-17(8)
C9	6299(4)	2643(3)	1796(5)	78(5)	40(3)	143(10)	37(6)	-16(11)	-8(8)
C10	6828(4)	3760(3)	2633(5)	75(5)	32(3)	131(10)	33(6)	-16(11)	-14(8)
C1'	3593(4)	5575(3)	2214(5)	78(5)	37(3)	126(9)	27(6)	11(11)	3(8)
C2'	4338(4)	6624(3)	3049(5)	70(5)	45(3)	138(10)	32(6)	-16(11)	-8(9)
C3'	3609(4)	7665(3)	3223(6)	77(5)	39(3)	176(11)	19(6)	-21(12)	-16(9)
C4'	2102(4)	7661(3)	2580(6)	76(5)	38(3)	167(11)	27(6)	-5(12)	5(9)
C5'	1336(4)	6627(3)	1820(6)	81(5)	42(3)	204(11)	36(6)	-29(12)	-17(9)
C6'	2065(4)	5591(3)	1630(6)	73(5)	44(3)	160(11)	16(6)	-28(12)	-14(9)
O3	2472(3)	3262(2)	275(4)	82(4)	46(2)	274(9)	32(5)	-131(9)	-84(7)
O5	6815(3)	683(2)	909)4)	107(4)	33(2)	268(8)	32(4)	-104(9)	-69(6)
O7	10609(3)	3359(2)	4188(4)	74(4)	50(2)	246(8)	30(4)	-88(9)	-58(7)
O4'	1322(3)	8663(2)	2725(4)	80(4)	40(2)	308(9)	50(4)	-64(9)	-55(7)
O(W)	8320(3)	-1204(2)	1735(4)	88(4)	54(2)	238(8)	35(5)	-82(9)	-40(7)

may be considerable, although the contribution of O3H is negligible. These hydroxyl groups tend to be substituted by sugars in naturally occurring anthocyanins. Fig.4 shows the π-bond order and the net charge density of atoms obtained by CNDO/2 molecular orbital calculation. These results well explain the above observations. The hydrogen bonding schemes of anthocyanidins are summarized in Fig.2. All the hydroxyl groups of pelargonidin are hydrogen bonded with water or bromine atom, however no intermolecular hydrogen bonding between the flavylium molecules such as the case in (II) is observed. The O7H and O4'H are directly hydrogen bonded with the bromine ion, whereas C5-O5H and C3-O3H are with the water molecules. Some charasteristic behaviors in the hydrogen bonding of anthocyanidins are observed in Fig.2. (1) The O4'H forms two hydrogen bonds as a donor and an acceptor. (2) The O7H of 3-hydroxyanthocyanidins hydrogen bond with the halogen ions, whereas in 3-deoxyanthocyanidins they hydrogen bond with the water molecules. (3) In 3-hydroxyanthocyanidins the hydroxyl groups at the 3- and 5- positions are not directly hydrogen bonded with halogen ions.

The crystal structure viewed along the a axis is shown in Fig.5. Pelargonidin molecules are stacked to form column along the c axis. A 3-dimensional hydrogen bond network stabilizes these columns.

The plane to plane interaction modes in anthocyanidins are shown in Fig.6. Two modes of molecular overlapping are observed. The one is related by the center of symmetry such as in (I) and (IV). The other is translation of the molecules such as in (II) and anhydrobase of (III)[7].

EXPERIMENTAL

The sample was obtained by the hydrolysis of pelargonin, the major pigment of the red flowers of Dahlia variabilis[8]. The crystals were prepared by slow evaporation from methanolic hydrobromic acid solution. They were dark-red needles elongated along the c axis. Oscillation and Weissenberg photographs showed that the crystals were triclinic space group P1 or $P\bar{1}$. The X-ray data were obtained on a Rigaku four-circle diffractometer with graphite monochromated Cu Kα radiation. A crystal with 0.005x0.005x0.2 mm in size was used. The lattice parameters were obtained by the least-squares fit of 2θ values of 25 reflexions centered on the diffractometer. The intensity data up to 153° in 2θ were obtained by 2θ/ω scan method with a scanning rate and range of $2°(2\theta)\mathrm{min}^{-1}$ and $(1+0.5(\alpha_1-\alpha_2))°$, respectively. Of 2855 independent reflexions measured, 2351 had intensities greater than 3σ(|Fo|) and were used for structure analysis. No correction was made for absorption. The crystallographic data are: $C_{15}H_{11}O_5$ Br·H_2O, F.W.=369, triclinic $P\bar{1}$, a=8.929(2), b=11.360(3), c=7.299(2)Å, α=95.0(5), β=93.61(5), γ=93.35(5)°, Z=2, D_x= 1.45 g·cm^{-3}, D_m=1.45 g·cm^{-3}, μ(Cu Kα)=24.5 cm^{-1}. The space group of $P\bar{1}$ was assumed and confirmed by a success of structure analysis. The bromine atom was located on a Patterson map. Successive Fourier maps revealed remaining carbon and oxygen atoms. The structural parameters were refined by the block-diagonal matrix least-squares method. Anisotropic thermal factors were applied to the Br, C and O atoms. All the hydrogen atoms were located on a difference Fourier map and their positional and isotropic thermal parameters were included in the refinement. The final R-value was 0.067 for observed reflexions. The weighting scheme at the final stage applied was $w=(Fmax/|Fo|)$ if $|Fo|>Fmax$, $w=1.0$ if $Fmax>|Fo|>Fmin$, $w=(|Fo|/Fmin)$ if $|Fo|<Fmin$, where Fmax and Fmin are 9.0 and 2.0, respectively. Atomic scattering factors were taken from Ref.9. The final positional and anisotropic thermal parameters are given in Table 1.

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