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Structure of Violdelphin, an Anthocyanin from Violet Flower of Delphinium hybridum

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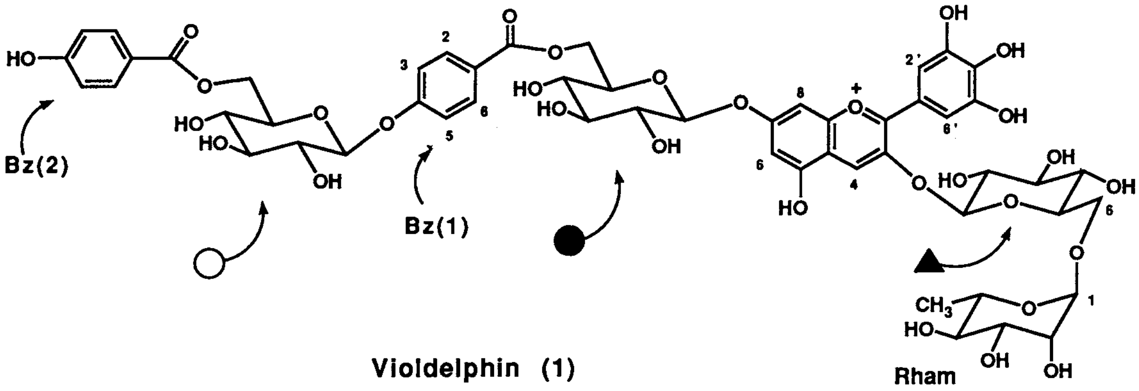
Structure of violdelphin was determined. It is a delphinidin derivative containing two molecules of p-hydroxybenzoic acid.

Delphinium flower is widely cultivated as one of the most famous horticultural plants in the world. In 1915, Willstätter isolated a pigment, delphinin, from the petals of Delphinium consolide and suggested the structure to be di-p-hydroxybenzoyldiglucosyldelphinidin.[1)] So far, it has been fairly rare that anthocyanins have a benzoic acid derivative as an acyl component in the molecule. In 1964 Horborne reported, however, that existence of p-hydroxybenzoyl group in the molecule is doubtful.[2)] Later, Asen et al. reported an anthocyanin isolated from larkspur cv Dark Blue Supreme to be delphinidin 3-di(p-hydroxybenzoyl)-glucosylglucoside.[3)] We have obtained from violet flowers of Delphinium hybridum a major anthocyanin that contains p-hydroxybenzoic acid but has a structure completely different from those reported above.

Fresh violet petals of Delphinium hybridum cv "Black Night" were frozen in liq. nitrogen, pulverized, and extracted twice with 3% aq. trifluoroacetic acid (TFA). The extracts were chromatographed on an Amberlite XAD-7 column by stepwise elution with 3% aq. TFA-CH_3CN and then purified by ODS-HPLC using $AcOH/CH_3CN/H_2O$ (20:25:55) containing 0.5% H_3PO_4 as the eluent to give, after replacing H_3PO_4 with TFA,[4)] violdelphin (1) TFA salt[5)] as a dark red powder.

FABMS of the pigment showed m/z 1175 (M^+). ^1H NMR indicated the presence of a delphinidin, two p-hydroxybenzoic acid moieties, and four hexoses. By means of COSY all protons of delphinidin nucleus and aromatic acyl groups were able to be assigned by taking the signal at 8.65 ppm as H-4. In HOHAHA spectra three of the hexoses were determined to be β-glucopyranosides from the vicinal couplings ($J_{1,2}$=7.5 Hz, $J_{2,3}$=$J_{3,4}$=$J_{4,5}$=9.5 Hz), and a remaining sugar was determined to be α-L-rhamnoside by comparison of the ^1H NMR with that of the sugar moiety of platyconin[6)] and violanin.[7)] Measurements of the difference NOE[8)] at room temp revealed the connection pattern of these parts. Irradiation of ▲-1 (5.36 ppm), ●-1 (5.38), and ○-1 (4.36) caused negative NOE at H-4, H-8, and 3 and 5 positions of a p-hydroxybenzoyl moiety, respectively, indicating that the glycosidic linkages of ▲, ●, and ○ are at 3[9)] and 7 positions of delphinidin nucleus, and 4 position of the benzoyl moiety, respectively. The position of attachment of rhamnose was determined by observation of NOE on ▲-6 when irradiated at the anomeric proton of rhamnose. Since protons of -CH_2- of ○ and ● were by 0.5 ppm lower field than that of ▲, 6 positions of ○ and ● are acylated. Thus, the structure of 1 was determined to be 7-O-(6-O-(4-(6-O-(4-hydroxybenzoyl)-β-D-glucopyranosyl)oxybenzoyl-β-D-glucopyranosyl)-3-O-(6-O-α-L-rhamnopyranosyl-β-D-glucopyranosyl)delphinidin.



Violdelphin (1)

References

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2) J. B. Harborne, Phytochem., 3, 151 (1964).
3) S. Asen, R. N. Stewart, and K. H. Norris, Phytochem., 14, 2677 (1975).
4) T. Kondo, Y. Nakane, H. Tamura, and T. Goto, Tetrahedron Lett., 26, 5879 (1985).

5) Violdelphin (1): UV λ_{max} (1%HCl-MeOH) nm (ε) 547 (18,600), 250 (22,800); ^{1}H NMR (500 MHz, in 8% TFA-d-CD_3OD at 26 °C) ppm (J) 8.65 (1H, s, H-4), 7.88 [2H, d, J = 9 Hz, Bz(1)-2 & 6], 7.80 (2H, s, H-2' & 6'), 7.39 [2H, d, J = 9 Hz, Bz(2)-2 & 6], 7.14 (1H, br.s, H-8), 6.82 [1H, d, J = 9 Hz, Bz(1)-3 & 5], 6.68 (1H, br.s, H-6), 6.47 [2H, d, J = 9 Hz, Bz(2)-3 & 5]; signals of the sugar moieties were assigned as follows:

Position	Chemical shift (ppm)			Coupling const.		Chem. shift	Coupl. const.	
	▲-glc	●-glc	○-glc	multi	J/Hz	rhamnose	multi	J/Hz
1	5.36	5.38	4.36	d	7.5	4.85	s	
2	3.90	3.70	3.45	dd	9.5, 7.5	3.96	br.s	
3	3.65	3.67	3.52	t	9.5	3.74	dd	9.5, 3
4	3.43	3.49	3.42	t	9.5	3.43	t	9.5
5	3.78	4.08	3.48	ddd	9.5, 8, 2	3.6-3.7	dq	9.5, 7
6a	4.17	5.02	4.61	dd	12, 2	1.28	d	7
6b	3.68	4.25	3.96	dd	12, 8			

NOE: ○-1 ↷ Bz(1)-3 & 5 (-9%), Rham-1 ↷ ▲-6 (-2%), ▲-1 ↷ H-4 (-9%), ●-1 ↷ H-8 (-13%), ●-1 ↷ H-6 (-2%).

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9) Also confirmed by NOE: ▲-1 ↷ H-2' & 6' (-2%), H-2' & 6' ↷ ▲-2 (-5%) (15 °C)

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