

PELARGONIDIN 3-MALONYLSOPHOROSIDE FROM THE RED ICELAND POPPY, *PAPAVER NUDICAULE*

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Key Word Index—*Papaver nudicaule*; Papaveraceae; acylated anthocyanin; pelargonidin 3-*O*-β-(6-*O*-malonyl)sophoroside; 6-*O*-malonylsophorose.

Abstract—Pelargonidin 3-malonylsophoroside was characterized as a flower pigment in a red form of the Iceland poppy, *Papaver nudicaule*.

An acid labile pigment **1** was extracted from fresh petals of a red cultivar of the Iceland poppy with MeOH–H₂O–HCOOH (900:100:1), chromatographed twice on polyamide with dilute formic acid (0.01–0.1 N) and precipitated at pH 3. Some pelargonidin 3-sophoroside (**2**) inevitably formed as a by-product during the purification procedure; in the plant it may be present in trace amounts.

The structure of **1** was partially deduced from elemental analysis, spectroscopic data [1] and the results of partial and total hydrolysis; methanolysis gave 1 mol of dimethyl malonate. A 4 hr oxidation with H₂O₂ at pH 2.8 followed by 100 hr treatment with Pd-sponge liberated a mixture of 6-*O*-malonylsophorose, 6-*O*-malonylglucose, sophorose and glucose, separated by paper electrophoresis and paper chromatography. The β-configuration of both glucose moieties, their [1 → 2]-linkage and the position of the malonyl group became evident from the ¹H NMR spectrum at 360 MHz in D₂O/DCI (pH 1.5) including nuclear Overhauser enhancement experiments; all the

proton resonances were completely resolved and most were of first order multiplicity (Table 1).

The *R_f* and spectral data of **1** and its degradation products are collected in Table 2. The malonated pigment **1** is hardly distinguishable from the known pelargonidin 3-sophoroside [2] by PC; this and the ease of hydrolysis may be the major reason why acylated flavonoids of this type have been overlooked in the past. There are only very few examples of malonated anthocyanins or flavones [3–8]. This is the first malonated anthocyanin to be fully characterized. Complete structures of malonyl hemiesters of two isoflavones [7] and a betacyanin [9] were known before; in all cases the malonyl group is attached to the C-6 of the glucose moiety. Paper electrophoresis (Table 2) provides an excellent means for distinguishing malonated pigments. Below pH 3, all anthocyanins behave as cations; the malonyl anthocyanin **1** moves slower than **2**. At pHs above 3, by contrast, the malonated compounds, such as **1**, are anionic whereas ordinary anthocyanins hardly move.

Table 1. Proton resonances of anthocyanins **1** and **2** in D₂O/DCI, pH 1.5 at 293 K (chemical shift in ppm from 3-trimethylsilyl sodium propionate-*d*₄ (TSP))

Pelargonidin protons			Protons of the internal glucose			Protons of the terminal glucose		
1	2		1*	2		1	2	
H-4	8.52	8.66	H-1''†	5.29	5.38	H-1'''‡	4.80	4.75
H-6§	6.48	6.49	H-2''	4.03	4.10	H-2'''	3.11	3.14
H-8§	6.59	6.64	H-3''	3.85	3.85	H-3'''	3.31	3.27
H-2'6'	8.10	8.12	H-4''	3.60	3.66	H-4'''	3.22	3.19
H-3'5'	6.98	6.87	H-5''	3.91	3.75	H-5'''	2.80	2.70
			H-6''A‡	4.67	4.08	H-6'''A	3.49	3.39
			H-6''B‡	4.39	3.90	H-6'''B	3.42	3.36

* The CH₂ protons of the malonyl moiety are not seen since rapid exchange with the deuterium of the solvent occurs.

† The β-configuration of the anomeric protons is ascertained from the coupling constant, *J* = 7.8 Hz.

‡ The attachment of the acyl group at –CH₂–O– is evident from the considerable deshielding of the H-6 protons in **1** as compared to those in **2**.

§ Assignments may be interchanged. Further details of these analyses will be published separately in *Helv. Chim. Acta*.

Table 2. Spectral, R_f and electrophoretic data

Compound	UV (MeOH/0.1 % HCl) $\lambda_{\max}(\epsilon)$	PC (R_f)*			PE (E_s)†	
		BAW	AHW	EPW	pH 2.4	pH 4.5
Pelargonidin	508 (28 950)					
3-malonylsophoroside	431 (11 300) 336 (3650) 269 (17 150)	0.33	0.72	—	−1.44	+0.11
Pelargonidin	509 (30 200)					
3-sophoroside	432 (12 000) 335 (4100) 270 (18 400)	0.31	0.68	—	−1.60	−0.08
Malonylsophorose		0.07		0.30		+0.37
Malonylglucose		0.16		0.27		+0.53
Sophorose		0.05		0.43	0	0
Glucose		0.13		0.55	0	0

* Solvents: BAW = *n*-BuOH–HOAc–H₂O (4:1:5); AHW = HOAc–conc HCl–H₂O (15:3:82) EPW = EtOAc–pyridine–H₂O (2:1:2).

† Electrolytes: pH 2.4 = 0.1 M formic acid; pH 4.5 = 0.05 M pyridinium formate. The E_s values are migrations relative to that of salicylic acid, E_s = 1.0 and glucose, E_s = 0, as markers.

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