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The blue anthocyanin pigments from the blue flowers of *Heliophila coronopifolia* L. (Brassicaceae)

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ABSTRACT

Six acylated delphinidin glycosides (pigments **1**–**6**) and one acylated kaempferol glycoside (pigment **9**) were isolated from the blue flowers of cape stock (*Heliophila coronopifolia*) in Brassicaceae along with two known acylated cyanidin glycosides (pigments **7** and **8**). Pigments **1**–**8**, based on 3-sambubioside-5-glucosides of delphinidin and cyanidin, were acylated with hydroxycinnamic acids at 3-glycosyl residues of anthocyanidins. Using spectroscopic and chemical methods, the structures of pigments **1**, **2**, **5**, and **6** were determined to be: delphinidin 3-*O*-[2-*O*-(β-xylopyranosyl)-6-*O*-(acyl)-β-glucopyranoside]-5-*O*-[6-*O*-(malonyl)-β-glucopyranoside], in which acyl moieties were, respectively, *cis*-*p*-coumaric acid for pigment **1**, *trans*-caffeic acid for pigment **2**, *trans*-*p*-coumaric acid for pigment **5** (a main pigment) and *trans*-ferulic acid for pigment **6**, respectively. Moreover, the structure of pigments **3** and **4** were elucidated, respectively, as a demalonyl pigment **5** and a demalonyl pigment **6**. Two known anthocyanins (pigments **7** and **8**) were identified to be cyanidin 3-(6-*p*-coumaroyl-sambubioside)-5-(6-malonyl-glucoside) for pigment **7** and cyanidin 3-(6-feruloyl-sambubioside)-5-(6-malonyl-glucoside) for pigment **8** as minor anthocyanin pigments. A flavonol pigment (pigment **9**) was isolated from its flowers and determined to be kaempferol 3-*O*-[6-*O*-(*trans*-feruloyl)-β-glucopyranoside]-7-*O*-cellobioside-4′-*O*-glucopyranoside as the main flavonol pigment.

On the visible absorption spectral curve of the fresh blue petals of this plant and its petal pressed juice in the pH 5.0 buffer solution, three characteristic absorption maxima were observed at 546, 583 and 635 nm. However, the absorption curve of pigment **5** (a main anthocyanin in its flower) exhibited only one maximum at 569 nm in the pH 5.0 buffer solution, and violet color. The color of pigment **5** was observed to be very unstable in the pH 5.0 solution and soon decayed. In the pH 5.0 solution, the violet color of pigment **5** was restored as pure blue color by addition of pigment **9** (a main flavonol in this flower) like its fresh flower, and its blue solution exhibited the same three maxima at 546, 583 and 635 nm. On the other hand, the violet color of pigment **5** in the pH 5.0 buffer solution was not restored as pure blue color by addition of deacyl pigment **9** or rutin (a typical flower copigment). It is particularly interesting that, a blue anthocyanin–flavonol complex was extracted from the blue flowers of this plant with H_2O or 5% HOAc solution as a dark blue powder. This complex exhibited the same absorption maxima at 546, 583 and 635 nm in the pH 5.0 buffer solution. Analysis of FAB mass measurement established that this blue anthocyanin–flavonol complex was composed of one molecule each of pigment **5** and pigment **9**, exhibiting a molecular ion $[M+1]^+$ at 2102 *m/z* ($C_{93}H_{105}O_{55}$ calc. 2101.542). However, this blue complex is extremely unstable in acid solution. It really dissociates into pigment **5** and pigment **9**.

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1. Introduction

The Brassicaceae is a large family of natural plant species and includes many important ornamental plants such as stock, wall flower, honesty, sweet alyssum and so on. Moreover, the range of their flower colors includes white, yellow, orange, red, violet and violet-blue, but a clear blue color is lacking except for that of *Heliophila* (cape stock in English). *Heliophila coronopifolia*, grown as an ornamental plant with attractive blue flowers, is endemic to cape areas.

In continuing the work on flower color variations caused by acylated anthocyanins in the Brassicaceae, the distribution of structurally complicated pelargonidin and cyanidin glycosides in the

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flowers of *Matthiola incana* (Saito et al., 1995, 1996), *Orychophragonus violaceus* (Honda et al., 2005), *Cheiranthus cheiri*, *Lobularia maritima* and *Lunaria annua* (Tatsuzawa et al., 2006, 2007, 2010), *Malcolmia maritima* (Tatsuzawa et al., 2008a), and *Iberis umbellata* (Saito et al., 2008) were previously reported. To the best of our knowledge, no report in the literature has described an anthocyanin study of the blue flowers of *H. coronopifolia*. Therefore, a study was carried out to elucidate the structures of anthocyanin pigments of the blue flowers of this plant. The anthocyanins in this flower were anticipated to be heavily acylated with molecules of hydroxycinnamic acids and malonic acid. In this paper, the structural elucidation of six new acylated delphinidin 3-sambubioside-5-glucoside and one acylated kaempferol glycoside isolated from the blue flowers of *H. coronopifolia* are reported, as well as a blue anthocyanin–flavonol complex comprising one molecule each of delphinidin 3-*p*-coumaroylsambubioside-5-malonylglucoside and kaempferol 3-feruloylglucoside-7-cellobioside-4′-glucoside.

2. Results and discussion

Eight anthocyanin peaks (pigments **1**–**8**) and one flavonol peak (pigment **9**) were observed in the MAW (methanol–acetic acid–water; 4:1:5, v/v/v) extract or 5% HOAc (acetic acid–water; 5:95, v/v) extract from the blue flowers of *H. coronopifolia* as major peaks by the HPLC analysis with monitoring at 530 nm for anthocyanins and at 350 nm for flavonols (Figs. 1 and 2). The proportions of anthocyanin peaks were 6.1% (pigment **1**), 6.4% (pigment **2**), 0.5% (pigment **3**), 1.1% (pigment **4**), 43.1% (pigment **5**), 29.2% (pigment **6**), 5.3% (pigment **7**) and 3.3% (pigment **8**), based on a percentage of the total absorbance of anthocyanin peaks. From the extract with 5% HOAc, these pigments were isolated and purified using the process described in a previous report (see Tatsuzawa et al., 2007, 2008a and Section 4.3.). The chromatographic and spectroscopic properties of these anthocyanins are summarized in Table 1, and also those of the flavonol glycoside were described in Section 4.4.2.

Acid hydrolysis of six anthocyanins (pigments **1**–**6**) resulted in delphinidin, glucose, xylose, and hydroxycinnamic acids in which *p*-coumaric acid was detected, respectively, in the hydrolysates of pigments **1**, **3** and **5**, caffeic acid in that of pigment **2**, and ferulic acid in those of pigments **4** and **6**. In addition, malonic acid was detected in the hydrolysates of pigments **1**, **2**, **5** and **6**. Similarly, acid hydrolysis of pigments **7** and **8** resulted in cyanidin, glucose, xylose, malonic acid and hydroxycinnamic acids (*p*-coumaric acid for pigment **7** and ferulic acid for pigment **8**).

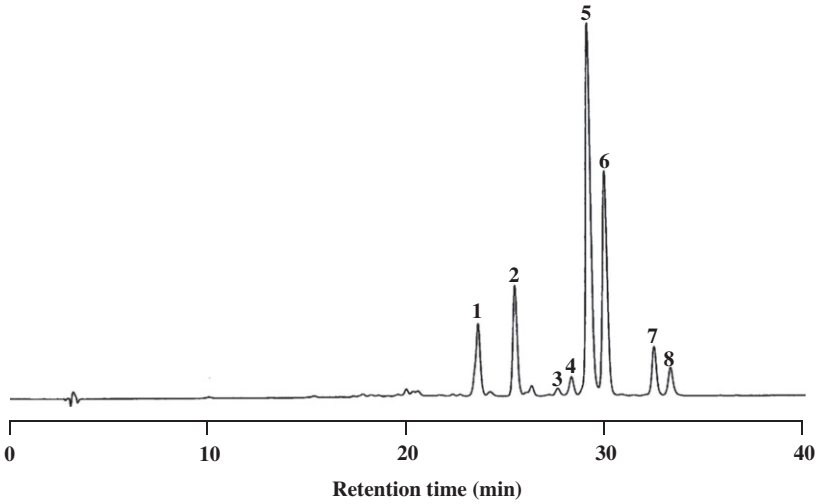

Fig. 1. HPLC profile for anthocyanins (530 nm) in the blue flower extract of *Heliophila coronopifolia* L. Pigments **1**–**8** are same as in Table 1.

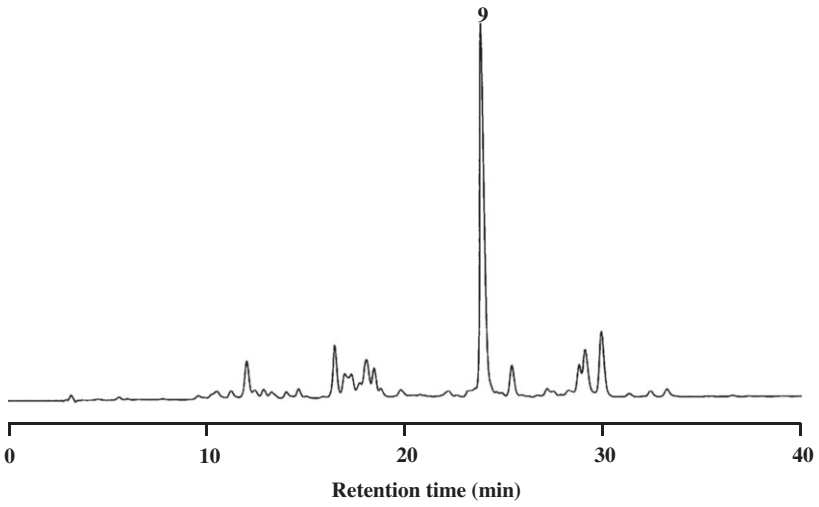

Fig. 2. HPLC profile (350 nm) for flavones and flavonols in the blue flower extract of *H. coronopifolia* L.

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