INTERNATIONAL WORKSHOP ON ANTHOCYANINS

"Research and Development in Anthocyanins"

2002

April 17-19, 2002
Paradise Wirrina Cove Resort
Adelaide, Australia

PROCEEDINGS
Polyacylated anthocyanins from Hebe

Luis Cabrita¹, Ulla Justesen², Nils Åge Frøystein¹ and Oyvind M. Andersen¹
¹Department of Chemistry, University of Bergen, Allégt. 41, N-5007 Bergen, Norway. ²Institute of Food Research and Nutrition, Danish Veterinary and Food Administration, Morkhej Bygade 19, DK-2860 Soborg, Denmark.

Four acylated anthocyanins were isolated from flowers of Hebe spp. On the basis of LC-MS (Liquid Chromatography–Mass Spectrometry) and NMR (Nuclear Magnetic Resonance) techniques, they were identified as (1) cyanidin 3-O-[2-O-(6-O-(E-coffeeyl)-β-glucopyranosyl)-6-O-(E-p-coumaroyl)-β-glucopyranoside]-5-O-β-glucopyranoside, (2) cyanidin 3-O-[2-O-(6-O-(E-p-coumaroyl)-β-glucopyranosyl)-6-O-(E-p-coumaroyl)-β-glucopyranoside]-5-O-β-glucopyranoside, (3) cyanidin 3-O-[2-O-(6-O-(E-coffeeyl)-β-glucopyranosyl)-6-O-(E-p-coumaroyl)-β-glucopyranoside]-5-O-[6-O-(malonyl)-β-glucopyranoside], and (4) cyanidin 3-O-[2-O-(6-O-(E-p-coumaroyl)-β-glucopyranosyl)-6-O-(E-p-coumaroyl)-β-glucopyranoside]-5-O-[6-O-(malonyl)-β-glucopyranoside]. Pigments 2 and 4 are novel compounds.
1. Introduction

The genus *Hebe* (Scrophulariaceae) comprises approximately 250 species and cultivars. It is centered on the New Zealand archipelago comprising around 120 species, the equivalent to 5% of the native angiospermic flora (Lange, 1999). *Hebe* (fig. 1) is also represented in South America, Australia and New Guinea.

2. Experimental

Isolation. Flowers from *Hebe speciosa*, *H. salicifolia* and *H. x andersonii* (200 g) were extracted with MeOH 0.1% TFA. The crude extract was concentrated, partitioned against hexane and ethyl acetate, washed on Amberlite XAD-7 and precipitated by diethyl ether. Isolation of purified anthocyanins was achieved upon combination of Sephadex LH-20 (size-exclusion) and semi-preparative HPLC (reverse phase) chromatography, affording pigments 1 - 6 (fig. 2).

It has been previously reported that at least pigment 5 was not an extraction artifact (Cabrita, 1999). However, a recent micro-extraction of *Hebe* flowers with three different solvents (methanol, ethanol and acetone with 0.1% TFA) followed by HPLC-DAD analysis did not support those previous findings.

3. Conclusions

Six anthocyanins were isolated and identified from flowers of *Hebe* spp. Pigments 1-2 were found to be based on cyanidin 3-sophoroside-5-glucoside acylated with coumaroyl-cafeoyl (1) and coumaroyl-coumaroyl (2) moieties. Pigments 3-4 and 5-6 were found to be the 5-malonylglucoside and 5-(methyl)malonylglucoside derivatives of 1 and 2, respectively.

4. References


Acknowledgments

LC gratefully acknowledges Fundação para a Ciência e Tecnologia, Portugal, for scholarships PRAXIS XXI BD/5290/95 and BPD/1639/2000. LC is very grateful to José Senna da Fonseca (Fundação Calouste Gulbenkian, Portugal) for plant material, Paula Pereira for photos of *Hebe*, and Prof. Fernando Santana (UNL/FCT) for a HPLC-DAD. The authors wish to thank Pia Knutsen (Institute of Food Research and Nutrition, Denmark) for valuable discussions.