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SHORT COMMUNICATION

BETACYANINS FROM *LAMPRANTHUS* SP. (AIZOACEAE)*†

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Abstract—Isolation and characterization of four betacyanins from flowers of *Lampranthus* sp. is reported. These pigments have been shown to be hydroxycinnamoyl derivatives of betanin and isobetanin.

INTRODUCTION

RECENT studies on betacyanins have shown that acylation is rather common in these pigments. Until now, acylated betacyanins have been isolated from plants of the Cactaceae, Amaranthaceae and Chenopodiaceae.[1,2] The present communication reports the isolation and characterization of four new acylated betacyanins from flowers of *Lampranthus* sp. (probably a garden hybrid).

METHODS AND RESULTS

Isolation and Characterization

The total betacyanin fraction was isolated by chromatography on strongly acid exchange resin; individual pigments were obtained from this fraction by chromatography on polyamide powder and by high voltage electrophoresis. General procedures for the characterization of acylated betacyanins have been described elsewhere;[1,2] these were used throughout this work.

Lampranthin-I and Isolampranthin-I

Lampranthin-I (λ_{max} 290, 320 and 538 nm; E_b's:‡ pH 2·4=0·40, pH 4·5=0·68), on alkaline hydrolysis under nitrogen, gave a mixture of betanin (I) and isobetanin (II), identified by direct chromatographic and electrophoretic comparison with authentic samples, and *trans*-ferulic and *trans*-*p*-coumaric acids. The molar ratio of ferulic to *p*-coumaric acid was determined by quantitative TLC and found to be 1 : 1. Since the recovery of the betanin–isobetanin mixture after alkaline hydrolysis was not quantitative, due to its relative lability, the ratio of deacylated glycosides to ferulic acid to *p*-coumaric acid was estimated from the absorptivity of lampranthin-I in the u.v. compared with that in the visible region of the spectrum and found to be 1 : 1 : 1.

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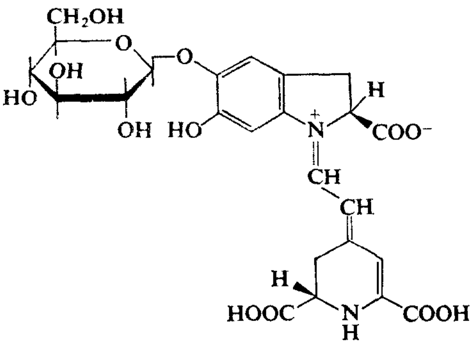
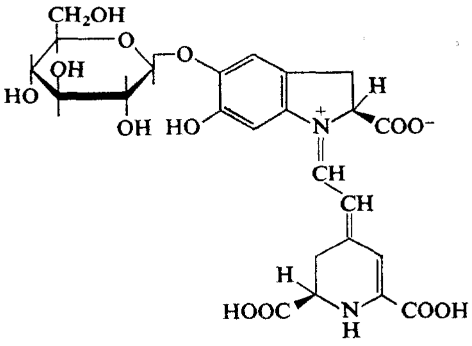
‡ E_b equals migration in paper electrophoresis relative to betanin.

[1] L. MINALE, M. PIATTELLI, S. DE STEFANO and R. A. NICOLAUS, *Phytochem.* **5**, 1037 (1966).

[2] L. MINALE, M. PIATTELLI and S. DE STEFANO, *Phytochem.* **6**, 703 (1967).



(I) Betanin



(II) Isobetanin

Diazomethane methylation of the pigment, followed by alkaline fusion of the methylated compound, gave 5-hydroxy-6-methoxyindole-2-carboxylic acid and shows that the phenolic hydroxyl group at position 6 of the aglycone is free in lampranthin-I.

Isolampranthin-I (λ_{max} 290, 320 and 538; E_b's: pH 2·4=0·40, pH 4·5=0·61) differs from lampranthin-I in yielding, on acid hydrolysis, isobetanidin rather than a mixture of betanidin and isobetanidin, the other chemical properties being identical. From this it can be inferred that lampranthin-I is a feruloyl-*p*-coumaroyl-betanin and isolampranthin-I is its C-15 diastereoisomer (feruloyl-*p*-coumaroyl-isobetanin.)

Lampranthin-II and Isolampranthin-II

Lampranthin-II (λ_{max} 288, 322 and 538 nm; E_b's: pH 2·4=0·17, pH 4·5=0·48) gave the same degradation products of lampranthin-I, differing only in the molar ratio of deacylated glycosides to ferulic to *p*-coumaric acid which was found to be 1:2:1.

Isolampranthin-II (λ_{max} 288, 322 and 538; E_b's: pH 2·4=0·17, pH 4·5=0·45) was shown to be C-15 diastereoisomer of lampranthin-II since it differs from the latter only in yielding on acid hydrolysis isobetanidin and not a mixture of betanidin and isobetanidin.

Therefore, lampranthin-II is a diferuloyl-*p*-coumaroyl-betanin and isolampranthin-II its C-15 diastereoisomer (diferuloyl-*p*-coumaroyl-isobetanin).

EXPERIMENTAL

Isolation of Pigments

Flowers of *Lampranthus* sp. (100 g) were homogenized in a blender with ice water (500 ml) and the homogenate centrifuged. The supernatant was acidified to pH 3 and percolated through a column of Dowex 50 (W-X2). After washing with 0·1 % HCl, the column was eluted with water. The eluate was concentrated to a small volume and chromatographed on a 1·6 × 50 cm powdered nylon column with 5 % citric acid in 50 % aqueous methanol. Three fractions were obtained, which emerged from the column after about 140, 500 and 2000 ml, respectively. Each fraction was freed from citric acid by resin treatment and taken to dryness. *Fraction* 1 was identified as a mixture of betanin and isobetanin by direct comparison with authentic compounds. *Fraction* 2, by preparative high-voltage electrophoresis (pH 4·5 (pyridine formate 0·05 M); potential gradient: 75 V/cm), gave two pigments (lampranthin-I and isolampranthin-I); *fraction* 3 similarly gave two bands, lampranthin-II and isolampranthin-II. All the pigments were eluted with water from the paper and freed from buffer by resin treatment.