

Laboratories, Inc., Elkhart, Indiana. I wish to thank Miss G. Armilei for her assistance in these studies.

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¹ Beers, jun., R. F., *Nature*, **177**, 790 (1956).

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Anthocyanidins of *Lochnera rosea*

In a survey of the anthocyanin flower pigments of plants growing in Trinidad¹, it was found that *Lochnera rosea* (*Vinca*) (*Apocynaceae*) contained an anthocyanin the aglycone of which was not identified. The fresh petals gave on chromatography a major glycosidic component of R_F 0.29 together with traces of two others R_F 0.23, 0.18 in the *n*-butanol/acetic acid/water (40 : 10 : 50) solvent used.

The pigments have now been further investigated. After acid hydrolysis a main pigment was found together with traces of two others. The two minor anthocyanidins were shown by chromatography to be petunidin and malvidin and to be derived from the two minor glycosidic components.

The major anthocyanidin was isolated as follows: fresh flowers (800 gm.) were extracted with 0.1 *N* hydrochloric acid (1.5 l.). The extract was made 2 *N* with hydrochloric acid and boiled for 15 min. After cooling the anthocyanidins were extracted with *n*-butanol (500 ml., then 250 ml.). The combined butanol extract was mixed with water (250 ml.) and light petroleum (2.5 l.) and the bottom layer added to a column of cellulose powder (40 × 3.7 cm.). The anthocyanidins were adsorbed on the top 5 cm. and were developed with *n*-butanol/2 *N* hydrochloric acid (top layer). The anthocyanidins and brown materials separated as discrete bands. This is a general and useful method of isolating anthocyanidins in quantity from crude extracts of flowers.

When the main anthocyanidin band had moved three-quarters of the way down, the column was sucked dry, extruded, and the band cut out. The pigment was extracted with methanol, the solution concentrated *in vacuo* to small volume and diluted with light petroleum. The precipitated pigment was dried *in vacuo*, dissolved in ethanol, and dry hydrochloric acid was passed in a 10 per cent concentration. On standing at 0°C. small regular cubic prisms (56 mgm.) of the main anthocyanidin separated. Found, after repeated recrystallization, C, 56.8; H, 4.7; OCH₃, 23.5: C₁₅H₁₇O₇Cl requires C, 56.8; H, 4.5; OCH₃, 24.4 per cent.

From colour properties² the substance obviously belongs to the delphinidin series, and from analysis it is a trimethyl delphinidin. It could not be separated from added hirsutidin on paper chromatography in several solvents (R_F in the Forestal³ solvent 0.73-0.74). Bearing in mind the possibility of methylation in the 5 instead of the 7 position, as in hirsutidin, the anthocyanidin is provisionally identified as hirsutidin, known previously only in *Primulaceae*⁴.

Three anthoxanthins also occur in the flowers: one has been identified certainly as kaempferol, and a second provisionally as quercetin; the third has not yet been identified. *Lochnera* thus joins the list of plants bearing unrelated anthocyanidins and flavonols in the flowers. Genetical investigations of flower colour are in progress.

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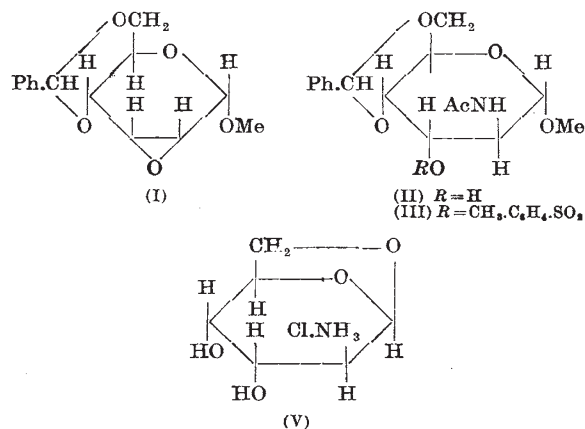
² Robertson A., and Robinson, R., *Biochem. J.*, **23**, 35 (1929).

³ Bate-Smith, E. C., *Biochem. J.*, **58**, 122 (1954).

⁴ Karrer, P., and Widmer, R., *Helv. Chim. Acta*, **10**, 758 (1927).

Characterization of 2-Amino-2-Deoxy-D-Altrose

THE action of methanolic ammonia on methyl 2:3-anhydro 4:6-*O*-benzylidene- α -D-allopyranoside (I) followed by acetylation (pyridine-acetic anhydride) of the isolated amino-compounds yielded, as the major product (45.7 per cent), after recrystallization from aqueous-methanol, methyl 2-acetamido 4:6-*O*-benzylidene 2-deoxy- α -D-altropyranoside (II), melting point 188-189°, $[M]_D + 218^\circ$ (acetone). (Found: C, 55.6, 55.8; H, 6.8, 6.7; N, 4.1. C₁₆H₂₁O₆N.H₂O requires C, 56.3; H, 6.7; N, 4.1 per cent).



The structure of (II) was indicated by the following observations.

(a) Elemental analysis.

(b) The infra-red absorption spectrum, in which the strong absorption at 1,725-1,749 cm.⁻¹, characteristic of the *O*-acetyl carbonyl group¹, was absent; but strong absorption at 1,651 cm.⁻¹ (N-acetyl carbonyl¹) was present. Methyl 3-acetamido 2-*O*-acetyl 4:6-*O*-benzylidene 3-deoxy- α -D-glucopyranoside, the well-studied² minor product of the above reaction, showed strong absorption at 1,726 cm.⁻¹ and 1,634 cm.⁻¹.

(c) With excess toluene-*p*-sulphonyl chloride in pyridine, II gave a mono-*O*-toluene-*p*-sulphonate (III), melting point 174° (decomp.), $[M]_D + 296^\circ$ (acetone). (Found: C, 58.0; H, 5.6; N, 3.0; S, 7.2. C₂₂H₂₇O₈NS requires C, 57.9; H, 5.7; N, 2.9; S, 6.7 per cent).

(d) Graded acidic hydrolysis³ of II removed the benzylidene residue and afforded amorphous methyl