tion and crystallization from MeOH afforded (II) m.p. 93–94°. (Found C, 82·73; H, 12·23; $C_{22}H_{38}O$ requires: C, 82·95; H, 12·03%.) TLC of the synthetic material with product obtained from I, over silica gel using light petroleum for elution showed the two to be identical. This was further confirmed by i.r. comparison of the synthetic and degradation products.

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CAMPANULACEAE

PLATYCONIN, A NEW ACYLATED ANTHOCYANIN IN CHINESE BELL-FLOWER, *PLATYCODON GRANDIFLORUM**

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Abstract—The anthocyanin in bluish-purple flowers of *Platycodon grandiflorum* A.DC. was crystallized in the form of chloride and identified as delphinidin 3-di-caffeoylrutinosido-5-glucoside.

A NUMBER of acylated anthocyanin based on delphinidin are known:[1] delphanin (violanin) in *Solanum*,[2,3] *Viola*[4] and *Petunia*,[5] awobanin in *Commelina*,[4] floridorin in *Iris*,[6] and delphinin in *Delphinium*,[7,8] although the last pigment may not be acylated as was originally suggested.[2]

A preliminary examination has revealed that a single anthocyanin is present in the bluish-purple flowers of Chinese bellflower ('kikyo' in Japanese).[9] For further study, this pigment was extracted from fresh petals of this plant, and precipitated in the form of lead

* Part LXIII in the Series "Studies on Anthocyanins"; for Part LXII, see *Proc. Japan Acad.* **46**, 535 (1970).

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salt as usual. Then, the blue lead salt was converted into the chloride by dissolving 5 per cent methanolic HCl, and the latter was precipitated with ether. The crystallization of this pigment was effected by 0·05 per cent ethanolic HCl. On acid hydrolysis, the pigment gave delphinidin, glucose, rhamnose and caffeic acid. Partial acid hydrolysis gave rise to the five intermediate glycosides, as follows: delphinidin 3-glucoside, 5-glucoside, 3-rutinoside, and 3-rutinosido-5-glucoside. In addition, four sugar components were liberated by acid hydrolysis of platyconin, i.e. glucose, rhamnose, rutinose and caffeoylrhamnose.

Deacylation with 4N NaOH for 45 min (in nitrogen) resulted in the production of caffeic acid and delphinidin 3-rutinosido-5-glucoside, and the latter was shown to be identical with the deacylation product of violanin (Table 1). The $E_{329}/E_{vis\ max}$ ratio (see Experimental) suggests that the pigment contains two molecules of caffeic acid.

TABLE 1. R_f VALUES OF PLATYCONIN AND OTHER DELPHINIDIN DERIVATIVES

Pigment	1% HCl	WAH*	BAW*	BUH*
Platyconin	0·14	0·33	0·01	0·07
Deacylated platyconin	0·26	0·53	0·03	0·08
Delphinidin 3,5-diglucoside (delphin)	0·04	0·28	0·02	0·08
Delphinidin 3-rutinosido-5-glucoside	0·27	0·53	0·04	0·10
Delphanin (violanin)	0·15	0·48	0·12	0·59

* On Tôyô-Roshi No. 51; solvent key: WAH, H_2O-HOAc–HCl (82:15:3, v/v); BAW, *n*-BuOH–HOAc–H_2O (4:1:5, v/v); BUH, *n*-BuOH–2N HCl (1:1, v/v).

So far as we know, this is the first description of the crystallization of caffeoyl-triglycoside of delphinidin occurring in the plant world. For the sake of convenience, the name *platyconin* is given to this new acylated anthocyanin.

EXPERIMENTAL

Plant Material

The deep bluish-purple petals of wild Chinese bell-flower were collected from the plants grown at the highland plain of Sugadaira in Nagano prefecture in late summer season. Also, the bluish-purple flowers of two cultivars called 'Wase' and 'Futu', were collected in the private garden of the one of us (N.S.) in mid-June. The pigments from these plant sources were found to be identical in all respects.

Isolation and crystallization

Freshly collected bluish-purple petals (2 kg) were immersed in 0·4% MeOH–HCl (3 l.) for 4 hr. A deep purple-red extract was filtered and an ethanolic solution of basic lead acetate was slowly added (1 l.), whereby the anthocyanin was completely precipitated from the filtrate as a blue lead salt (12 g). This was treated with cold EtOH–HCl, and the anthocyanin chloride in solution was precipitated with ether (3 vol.). This crude crop of amorphous pigment was dissolved in 50% EtOH containing 0·05% HCl, and kept at 0° for several days. The pigment chloride was gradually separated in the form of straight-cut, red needles. The recrystallization was repeated twice in the same way. Yield ca. 0·5 g (corresponding to 0·025% of the fresh petals).

Characterization of platyconin chloride

The crystalline chloride had m.p. 193–195° (decomp.); u.v. spectrum: λ_{max} 287, 329 (broadband) and 549 nm in EtOH contg 0·1% HCl; $E_{440}/E_{vis\ max}$ 13%, $E_{329}/E_{vis\ max}$ 90%; the i.r. absorption characteristic for carbonyl group: 1685 cm^{-1} (KBr). (Anal. Calc. for $C_{51}H_{53}O_{27}Cl \cdot 10H_2O$: C 46·63, H 5·60%. Found: C 46·61, H 5·55%.)

Platyconin and its hydrolysis products were identified by standard techniques.[3,10,11] R_f values are given in Table 1. In the H_2O_2 degradation of platyconin, the caffeic acid residues were destroyed and only rutinose was recovered (c.f. Ref. 2).

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COMPOSITAE

TRITERPENOIDS AND AROMATIC COMPONENTS OF DEERTONGUE LEAF

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Abstract—Lupeol and α-amyrin, together with the corresponding palmitates and acetates, and lupenone were isolated from dried deertongue leaves. A low-boiling fraction from the total extract contained 2,3-benzofuran, dihydrocoumarin, and coumarin.

INTRODUCTION

THE PLANT referred to as deertongue was initially regarded as a member of the genus *Liatris* and later as a *Trilisa* species. However, it has most recently been united to the genus *Carphephorus* and the correct name according to Hebert[1] is *C. odoratissimus* (J. F. Gmel) Hebert. The oleorosin from this plant, due to its high coumarin content, is frequently used as a fixative in perfumery. The roots were for a long time noted for their medicinal properties, and extracts from the dried leaves were used in the food flavouring industry prior to 1952 when a general ban was imposed on coumarin-containing products. The dried leaves are still however used as a flavouring additive in certain blends of tobacco and for this reason we have initially examined the volatile and low-polarity components from this source.

RESULTS

Commercially available deertongue leaf, on extraction with hexane, furnished a dark green viscous gum (3%), and further extraction with ether gave material of similar appearance (3%). Gradient chromatography (light petroleum–isopropyl ether) of the hexane soluble part of the extract yielded five fractions, the most polar of which was identified as coumarin. Thin

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