

## Pelargonidin Glycosides in Fruits

Pelargonidin glycosides have hitherto been found quite rarely as fruit pigment. HARBORNE<sup>1</sup> has pointed out that in fruits cyanidin occurs to the extent of about 70% and delphinidin is fairly frequent, but the occurrence of pelar-

Table I. Rf values and absorption maxima of anthocyanins found in the fruits and their aglycones

Pigment	Rf values in			Spectral max. in		
	BuH <sup>a</sup>	AAH <sup>a</sup>	BAW <sup>b</sup>	MeOH/HCl (nm)		
PMG <sup>b</sup>	0.50	0.49	0.45	278	431	506
PRG <sup>b</sup>	0.52	0.57	0.39	278	430	507
PXG <sup>b</sup>	0.66	0.70	0.40	276	431	506
CMG <sup>b</sup>	0.38	0.40	0.28	281		524
CRG <sup>b</sup>	0.42	0.56	0.26	282		526
CXG <sup>b</sup>	0.48	0.65	0.25	281		524
Pelargonidin	0.98	0.30	—	270	429	522
Cyanidin	0.87	0.18	—	278		532

<sup>a</sup> BuH: *n*-BuOH - HCl - H<sub>2</sub>O (7:2:5); AAH: AcOH - HCl - H<sub>2</sub>O (3:1:8). <sup>b</sup> See text for composition.

chloric acid were made in order to confirm their components, i.e., anthocyanidins and sugars, and also their mode of linkage. Glucose, rhamnose and xylose were identified by paper chromatography in 2 solvents. Their R<sub>f</sub> values were 100, 205 and 155 in *n*-BuOH - pyridine - H<sub>2</sub>O (6:4:3), and 100, 190 and 140 in EtOAc - pyridine - H<sub>2</sub>O (12:5:4) respectively. The spots were discerned by either of the reagents, alkaline silver nitrate and aniline hydrochloride. Aglycone, pelargonidin, was further confirmed by potash fusion to degrade into phloroglucinol and *p*-hydroxybenzoic acid. R<sub>f</sub> values of these degradation products were 0.73 and 0.93 in *n*-BuOH - AcOH - H<sub>2</sub>O (6:1:2) (BAW), and 0.16 and 0.88 in C<sub>6</sub>H<sub>6</sub> - AcOH - H<sub>2</sub>O (125:72:3) (BzA). The colors with sulphanic reagent were brown and yellow respectively.

On the other hand, except for *Skimmia japonica* THUNB. var. *repens*, cyanidin glycosides have been shown to be contained in the fruits. They were 3-monoglucoside (CMG), 3-rhamnosylglucoside (CRG) and 3-xylosylglucoside (CXG) of cyanidin. Their chemical structures were determined by the same way as above. The potash fusion of aglycone, cyanidin, revealed that two decomposition products behaved identically with authentic phloroglucinol and protocatechuic acid. R<sub>f</sub> values of the latter

Table II. Distribution of anthocyanins in the fruits

Species	PMG <sup>a</sup>	PRG <sup>a</sup>	PXG <sup>a</sup>	CMG <sup>a</sup>	CRG <sup>a</sup>	CXG <sup>a</sup>
<i>Chloranthus glaber</i> (THUNB.) MAKINO	—	6	—	—	4	—
<i>Nadina domestica</i> THUNB.	1	—	6	—	—	3
<i>Skimmia japonica</i> THUNB. var. <i>repens</i> (NAKAI) OHWI	4	6	—	—	—	—
<i>Ilex latifolia</i> THUNB.	—	—	8	—	—	2
<i>Ilex integra</i> THUNB.	—	—	8	—	—	2
<i>Ilex serrata</i> THUNB.	—	—	9	—	—	1
<i>Aucuba japonica</i> THUNB.	—	—	7	—	—	3

<sup>a</sup> See text for composition.

gonidin in fruits is unusual; it has been known only in fruits of *Fragaria*<sup>2</sup>, *Rubus*<sup>3</sup>, *Passiflora*<sup>4</sup> and *Nerine*<sup>1</sup>. Pelargonidin and delphinidin glycosides occur rather commonly in flowers.

Recently, the author has reported that the fruit coat of *Ilex aquifolium* contains the 3-xylosylglucosides of both pelargonidin and cyanidin, which are present nearly in the ratio of 1:1<sup>5</sup>. Now, as a result of further survey, the fruits shown in Table II have been found to contain pelargonidin glycosides by means of paper chromatographic technique. Therefore, pelargonidin seems not always to be a rare pigment in fruits. And it is noticeable that in most cases pelargonidin is accompanied by cyanidin and these 2 pigments present in fruits tend to be of the same glycosidic type, and also that the 3-xylosylglucosides are frequently encountered in fruits. This fact reminds the author of the previous finding of the 3-xylosylglucoside of delphinidin also in the fruits of *Daphniphyllum macropodum*<sup>6</sup>.

In the present experiment, 3 kinds of pelargonidin glycoside were found. They were 3-monoglucoside (PMG), 3-rhamnosylglucoside (PRG), and 3-xylosylglucoside (PXG) of pelargonidin. The pigments were separated by a large scale paper chromatography. Their R<sub>f</sub> values and absorption maxima in 0.01% methanolic hydrochloric acid are summarized in Table I. Complete and partial hydrolyses of the pigments with dilute hydro-

were 0.87 in BAW and 0.64 in BzA. The color with sulphanic reagent was tan. In Table II, the ratio of individual pigments in samples was estimated by the spot size on the paper chromatograms in three solvents.

*Zusammenfassung.* Pelargonidin-Derivate, welche als Fruchtfarbstoffe bisher selten festgestellt worden sind, wurden in den Früchten von sieben Pflanzenarten gefunden und auf Grund papier-chromatographischer Analyse als 3-Monoglucosid, 3-Rhamnoglucosid und 3-Xyloglucosid von Pelargonidin identifiziert. Daneben wurden in den obenerwähnten Früchten auch drei Sorten von Cyanidin-Derivaten des ganz identischen Glycosid-Typs gefunden.

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<sup>1</sup> J. B. HARBORNE, *Comparative Biochemistry of the Flavonoids* (Academic Press, New York 1967).

<sup>2</sup> E. SONDHEIMER and C. B. KARASH, *Nature*, Lond. 178, 648 (1956).

<sup>3</sup> J. B. HARBORNE and E. HALL, *Phytochemistry* 3, 453 (1964).

<sup>4</sup> J. S. PRUTHI, R. SUSHEELA and G. LAL, *Food Res.* 26, 385 (1961).

<sup>5</sup> N. ISHIKURA, *Bot. Mag. Tokyo*, 84, 113 (1971).

<sup>6</sup> M. SHIBATA and N. ISHIKURA, *Bot. Mag. Tokyo* 77, 277 (1964).