

Anthocyanidins from Hips of *Rosa pimpinellifolia* L.Anthocyanidiny z šípků *Rosa pimpinellifolia* L.

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Abstract — KONČALOVÁ M. N. (1971): Anthocyanidins from hips of *Rosa pimpinellifolia* L. — Preslia, Praha, 43 : 198—201. — Aglycons of some anthocyanins from hips of *Rosa pimpinellifolia* L. and its derived hybrids were determined by means of a comparative chromatographic analysis. The use of this method for the solution of some taxonomic questions of the genus *Rosa* is discussed.

Introduction

The great colour variety of rose flowers attracted not only botanists, but also chemicians already during the first years of this century. WILLSTÄTTER et NOLAN (1915a) determined the main pigment from dry petals of *Rosa gallica* L. and from that time this rose has served as the most abundant source of cyanin or cyanidin for different comparative works.

In forties, when anthocyanins were studied with a great interest, ROBINSON et ROBINSON (1934) identified many of these pigments using a number of qualitative tests based on the chemical behaviour of anthocyanins and anthocyanidins in different plants. Among them also flower extracts of polyantha roses were investigated. They found pelargonin and cyanin in the orange red 'Gloria Mundi' and 'Prince of Orange' and only cyanin in the blue red flowers of 'Veilchen Blau'.

More precise analysis of anthocyanins and their compounds was made possible by chromatography (HARBORNE 1958). A third major anthocyanin peonin was discovered in *Rosa rugosa* THUNB. and derived varieties e.g. 'Roseraie de L'Hay' (HARBORNE 1961). Peonin had previously been found only in peony blooms (WILLSTÄTTER et NOLAN 1915b).

Anthocyanins and their sugar components were studied in detail by HARBORNE (1962; 1963a, b). About one hundred rose species and cultivars were also investigated and anthocyanins and their glycosidic patterns from petals were determined, but unfortunately without any taxonomic notes. As far as we know anthocyanins from roses have been investigated up till now only in flowers, while in the case of other plants from the family *Rosaceae*, anthocyanins have been analysed only from fruits (*Rubus*, *Prunus*, *Malus*, *Fragaria*) or from bark (*Pyrus*) — HARBORNE 1963b.

The red colour of hips is mostly due to the presence of carotenoids, but *Rosa pimpinellifolia* L. (syn. *R. spinosissima* L.) the so called Burnet Rose or Scotch Rose forms hips of very dark purple black colour. The simple colour reactions of the juice from these hips clearly showed the presence of a great amount of anthocyanins. Therefore we tried to find more detailed data about the character of these compounds by chromatographic analysis.

Material and methods

The material used for analysis was the dried flesh from hips of wild roses, their spontaneous hybrids and cultivated varieties of rose hybrids especially so called shrub roses. Part was collected from the rosarium of the Botanical Institute of the Czechoslovak Academy of Sciences at Průhonice. It contains collections of Dr. Ivan Klášterský from the years 1935–1970 and is marked in the following list by R. The second part of hips has its origin in the collection of the Research Institute of the Ornamental Horticulture at Průhonice and is marked VU in the list below. The hips were picked on 28th October 1970 after some mild morning frosts. They were dried at room temperature about three weeks.

The list of used material

1. *Rosa pimpinellifolia* L. var. *pimpinellifolia* (syn. *R. pimpinellifolia* L. var. *typica* CHRIST), R 316. — The seedling was acquired in 1949 as a gift from Josef Vik from the Municipal Nursery at Dáblice. Purple black hips are very rare, generally with no seeds inside.

2. *Rosa pimpinellifolia* L., R 317. — This plant has the same origin as the first one (under No 1). Purple black hips are abundant.

3. *Rosa pimpinellifolia* L., VU II/19.

4. *Rosa pendulina* L. — The mixture of hips from 9 plants. These shrubs were transplanted from natural habitats (Železné hory Mts., C. Bohemia; Doupovské hory Mts., NW. Bohemia) to the rosarium in 1951.

5. *Rosa* × *reversa* WALDST. et KIT. (a spontaneous hybrid between *Rosa pendulina* L. and *Rosa pimpinellifolia* L.). — The hips were collected from three shrubs R 258a, 258b, 259 of the identical habit. In 1950 all the three individuals were transplanted to the rosarium from the top of the mountain Tanád near Banská Štiavnica (Slovakia), where they had grown among the supposed parental plants. Flowers are dark pink, hips are purple.

6. *Rosa* × *reversa* WALDST. et KIT., VU II/11.

7. *Rosa* (shrub) 'Frühlingsmorgen', VU XII/18, 19, 20. — The origin of this shrub rose is given by Kordes Co in 1942 as (*R.* 'E. G. Hill' × *R.* 'Catharine Kordes') × *R. pimpinellifolia* L. var. *altaica* Sér. (sec. MCFARLAND 1965). Simple flowers are pink with yellow center. Huge red hips were collected from three shrubs.

8. *Rosa* (shrub) 'Frühlingsduft', VU XIV/7, 8, 9. — The origin of this shrub rose is given by Kordes Co in 1949 as *R.* 'Joanna Hill' × *R. pimpinellifolia* L. var. *altaica* Sér. (sec. MCFARLAND 1965). Golden flowers with pink tinge are big, sometimes doubled. Hips with dark red colour were collected from three shrubs.

9. *Rosa* (shrub) 'Frühlingszauber', VU XVI/4, 5, 6. — The origin of this shrub rose is given by Kordes Co in 1942 as (*R.* 'E. G. Hill' × *R.* 'Catharine Kordes') × *R. pimpinellifolia* L. var. *altaica* Sér. (sec. MCFARLAND 1965). Pink flowers are semidoubled, huge dark red hips were examined from three shrubs.

Anthocyanins from the following plants were extracted for comparison:

10. *Rosa* (polyantha-hybrid) 'Chatter', petals.

11. *Rosa* (polyantha-hybrid) 'Fortschritt', petals.

12. *Pelargonium*, cultivated varieties, petals.

13. *Cyclamen*, cultivated varieties, petals.

14. *Fuchsia*, cultivated varieties, petals.

15. *Sambucus nigra* L., fruits.

16. *Pyracantha coccinea* ROEM., fruits.

17. *Chrysanthemum hortuorum* hort. (= *Ch. koreanum* hort. × *Ch. indicum* L.), flowers.

18. *Salvia splendens* SELLOW, cultivated varieties, flowers.

With regard to the preliminary character of this work and to the late date of collecting hips the identification of glycosidic patterns has been given up for the time being. Anthocyanins were extracted by 1% methanolic HCl. Hydrolysis with 20% HCl was followed by repeated extraction by isoamylalcohol. Anthocyanidins were separated by paper chromatography (Whatman 1) in two different solvent systems:

a) glac. acetic acid : conc. HCl : water = 30 : 3 : 10 (HARBORNE 1967).

b) amylalcohol : conc. HCl : water = 5 : 1 : 1 (HAYASHI et al. 1953).

Thin layer chromatography (Silicagel G) was also used (solvent system ethylacetate : formic acid : water = 85 : 6 : 9, Hess et MEYER 1962). The spots of anthocyanidins were distinguished under UVL and daylight by their R_f values and characteristic colours (HARBORNE 1958). Delphinidin, cyanidin and pelargonidin were also identified by direct comparison with anthocyanidins from the determined sample of *Salvia splendens* SELLOW, acquired as a gift from J. HENDRYCHOVÁ from the Faculty of Science, Charles University in Praha.

Results and discussion

The results are summarized in Tab. 1 and 2. Only the hips of *Rosa pendulina* showed an absolute absence of anthocyanidins. Berries of *Sambucus* and hips from *Rosa pimpinellifolia* and *Rosa reversa* as well as petals of polyantha roses are very rich sources of cyanidin. On the other hand petals from *Cyclamen*, *Fuchsia* and *Pelargonium* contain a very small amount of cyanidin. Identifi-

Tab. 1. — The occurrence of anthocyanidins* in the investigated roses

No.	Name	Organ	Dp	Cy	Mv	Pn	Pg
1	<i>R. pimpinellifolia</i> R 316	hips	—	+	—	+	+
2	<i>R. pimpinellifolia</i> R 317	hips	—	+	—	—	—
3	<i>R. pimpinellifolia</i> VU	hips	—	+	—	—	—
4	<i>R. pendulina</i> R	hips	—	—	—	—	—
5	<i>R. × reversa</i> R	hips	—	+	—	—	—
6	<i>R. × reversa</i> VU	hips	—	+	—	—	—
7	<i>R.</i> 'Frühlingsmorgen' VU	hips	—	+	—	—	—
8	<i>R.</i> 'Frühlingsduft' VU	hips	—	+	—	—	—
9	<i>R.</i> 'Frühlingszauber' VU	hips	—	+	—	—	—
10	<i>R.</i> 'Chatter'	petals	—	+	—	—	—
11	<i>R.</i> 'Fortschritt'	petals	—	+	—	+	+

*) Dp = delphinidin; Cy = cyanidin; Mv = malvidin; Pn = peonidin; Pg = pelargonidin

fication was clear only in fresh extracts. Up to the present time we have not found any data about the occurrence of cyanidin in *Cyclamen*, *Fuchsia* and *Pelargonium*. A small amount of delphinidin was identified in petals from *Fuchsia* and *Cyclamen*.

Regarding anthocyanidins from the petals of polyantha-hybrid roses we found a great amount of cyanidin in both samples. Moreover, the fresh extract of polyantha-hybrid rose 'Fortschritt' (No 11) also contained peonidin and pelargonidin in very small quantities. No spots corresponding to peonidin and pelargonidin were obtained if extracts had been stored more than two weeks before chromatographic analysis.

It seems to be interesting that the same anthocyanidins occur in the hips of *Rosa pimpinellifolia* R 316 (sample No 1), while in hips of *R. pimpinellifolia* R 317 and VU II/19 (under No 2 and 3) only cyanidin was iden-

Tab. 2. — The occurrence of anthocyanidins*) in the investigated plants

No.	Name	Organs	Dp	Cy	Mv	Pn	Pg
12	<i>Pelargonium</i>	petals	—	+	—	+	+
13	<i>Cyclamen</i>	petals	+	+	+	+	—
14	<i>Fuchsia</i>	flowers	+	+	+	+	—
15	<i>Sambucus nigra</i>	fruits	—	+	—	—	—
16	<i>Pyracantha coccinea</i>	fruits	—	+	—	—	—
17	<i>Chrysanthemum hortuorum</i>	flowers	—	+	—	—	—
18	<i>Salvia splendens</i>	flowers	+	+	—	—	+

*) Dp = delphinidin; Cy = cyanidin; Mv = malvidin; Pn = peonidin; Pg = pelargonidin

tified. The hybrid character of *R. pimpinellifolia* R 316 could be expected. Five year's observation has shown that the flowering time of this shrub is in the average ten days later than that of other shrubs of *R. pimpinellifolia* growing under the same conditions. This plant does not flower very much and brings very few hips, commonly with no seeds inside. Also the cytological observation (KONČALOVÁ 1971) supports the hypothesis of the hybrid origin of the rose in question ($2n = 21$).

In hips of the hybrid *R. × reversa* cyanidin was only found. Despite the deep red colour of the flowers of *Rosa pendulina*, the hips do not contain any anthocyanins. The analysis of the extract from hips of the cultivated hybrids of *Rosa pimpinellifolia* var. *altaica* (with huge dark purple hips) showed similar results as were obtained in the case of *Rosa × reversa*. The colour of the hips from all these cultivated hybrid forms which we examined (under No 7, 8, 9) was from deep orange to dark red, but it was not possible to assume the presence of anthocyanins from their appearance as was possible, for example, in the intermediate *R. reversa*. But with the aid of chromatography it is easy to detect the presence of cyanidin in the hips of all these hybrids. As the only rose species with dark purple hips containing anthocyanins is *R. pimpinellifolia* we assume that it may be possible to identify the parentship of *Rosa pimpinellifolia* by means of chromatographic analysis of the pigment from the hips of rose hybrids.

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Souhrn

Pomocí srovnávací chromatografické analýzy byly zjištěny v šípcích *Rosa pimpinellifolia* L. a v šípcích jejich hybridů aglykony některých anthokyanů a je diskutována použitelnost této metody při řešení některých taxonomických otázek rodu *Rosa*.

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