

PHENOLIC COMPOUNDS OF THE LEAVES

OF *Vaccinium arctostaphylos*

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We have previously [1] reported the isolation from the leaves of *Vaccinium arctostaphylos* L. (Caucasian whortleberry) of caffeic, chlorogenic, neochlorogenic, and 3- and 5-p-coumaroylquinic acids, and also 3,5-dicaffeoylquinic acid. Continuing an investigation of the qualitative composition of the leaves, we have isolated six phenolic substances (Table 1). The fresh leaves of *V. arctostaphylos* were fixed with liquid nitrogen and were extracted with water at 50°C. The extractive substances were separated on polyamide and cellulose columns.

**Cryptochlorogenic Acid.** The products of alkaline and enzymatic hydrolysis were caffeic and quinic acids. On acid hydrolysis, in addition to caffeic acid the structural isomers chlorogenic, neochlorogenic, and 1-caffeoylquinic acids were formed.

**Caffeoyl- and p-Coumaroylarbutins.** Alkaline hydrolysis formed arbutin and also caffeic and p-coumaric acids, respectively. On acid and enzymatic cleavage, hydroquinone, glucose, and caffeic and p-coumaric acids were detected. In neither case could the position of the acyl fragment be established because of transesterification.

**1-p-Coumaroylgalactoglucose.** The compound is readily cleaved by alkalis and by  $\beta$ -amylase to p-coumaric acid, D-galactose, and D-glucose. The considerable bathochromic shift of the maximum of the long-wave band in the UV spectrum in the presence of alkali (see Table 1) shows the presence of a free phenolic hydroxy group and of the p-coumaric acid in the form of an ester [2]. The negative reaction with aniline phthalate shows the probable position of the p-coumaric acid at C-1 of the carbohydrate component.

TABLE 1

Compound	$R_f^*$	Fluorescence in UV light (~366 nm)			Diazot. sulf. acid	UV spectrum ( $\lambda_{max}$ , nm)	
		with-out add.	+NH <sub>3</sub>	+KOH		eth-anol	+KOH
Cryptochlorogenic (4-caffeoyl-quinic) acid	0,60	Blue	Blue-green	Yellow	Yellow-brown	245 (295) 326	255 380
Caffeoylarbutin	0,90	"	"	"	Violet	245 (299) 328	260 385
Rosmarinic acid	0,40	"	"	"	Yellow-brown	287 328	295 380
p-Coumaroylarbutin	0,78	—	Blue	Blue	Violet	(300) 312	(312) 360
p-Coumaroylgalactoglucose	0,85	—	"	—	Pink	(298) 312	250 365
Arbutin	0,88	—	—	—	Violet	285	300

\*2% acetic acid.

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Alkaline hydrolysis was performed with 0.1 N KOH solution in an atmosphere of nitrogen by heating in the boiling water bath for 30 min, acid hydrolysis with 5% sulfuric acid heating in the boiling water bath for 1 h, and enzymatic hydrolysis by incubation with  $\beta$ -amylase at 37°C for 20 h.

#### LITERATURE CITED

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