Flavonoids of *Arctostaphylos uva-ursi* (Ericaceae)

The genus *Arctostaphylos* (Ericaceae) contains 25 species, the majority of which are restricted in distribution to Western North America. *Arctostaphylos uva-ursi* (L.) Spreng, (bearberry) is widely distributed in North America, especially Canada, and has been shown to be of two cytologically and morphologically distinguishable varieties (var. *adenotricha* Fern. and Macbr. $2n = 26$ and var. *coactilis* Fern. and Macbr. $2n = 52$).[1,2] *A. uva-ursi* var. *adenotricha* would appear to be restricted in its distribution to North America, whereas var. *coactilis* is also found in Europe and Asia[1-3].

Recent studies have demonstrated that a third variety of *A. uva-ursi* is restricted in its distribution to elevated regions of the Canadian Rockies and Alaska[2]. This variety has the same chromosome number as var. *coactilis* but is morphologically distinct, and is referred to in this paper as 'stipitate'.

As part of a continuing study of this species complex, 50 samples of both vars. *adenotricha* and *coactilis*, as well as 6 samples of the rarer 'stipitate' form were assayed for flavonoids.

Fresh leaves of each variety of *Arctostaphylos uva-ursi* were extracted with 80% ethanol. Excessive chlorophyll was removed with multiple aliquots of petrol-ether. Two-dimensional paper chromatography of hydrolyzed and non-hydrolyzed extracts showed a total of eleven flavonoids. The major aglycone present was quercetin and the minor aglycone myricetin. Standard methods were used to establish flavonoid identities[4,5] (UV, Rf's, fluorescence, spectrophotometry and direct comparison with known standards).

Five quercetin monoglycosides were identified after purification and hydrolysis (Table) and 2 myricetin monoglycosides as well as 2 quercetin diglycosides. It is of interest to note that all the flavonoids encountered are flavonols showing a somewhat primitive biochemical profile[6]. The absence of certain flavonoids in the stipitate form (myricetin 3–0 arabinoside, quercetin 3–0 arabinoside and quercetin 7–0 glucoside) may well indicate a phylogenetic difference between the latter and its more commonly distributed relatives.

The restricted phytogeographic distribution of the 'stipitate' form especially its occurrence in suspected glacial refugia of the Rocky Mountains and Alaska[7], has led the author to suspect that biochemical markers, such as flavonoids, might be of value in establishing plant refugial boundaries. Such studies are at present under way.

Résumé. Dans trois variétés d'*Arctostaphylos uva-ursi*, j'ai trouvé les flavanoides suivants: arabinoside-3, glucoside-3, galactoside-3, diglucoside-3, rutinoside-3, rhamnoside-3, glucoside-7-quercetine and arabinoside-3, glucoside-3-myricetine. J'ai déduit une corrélation entre la distribution limitée de certains d'entre ces flavonoides et les localités, en Amérique du Nord qui ont échappé a la glaciation.

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Distribution of flavonoids in *Arctostaphylos uva-ursi*

	Varieties		
	adenotricha	coactilis	stipitate
Myricetin	+	+	+
M 3-0 arabinoside	+	+	—
M 3-0 glucoside	+	+	+
Quercetin	+	+	+
Q 3-0 galactoside	+	+	+
Q 3-0 glucoside	+	+	+
Q 3-0 rhamnoside	+	+	+
Q 3-0 arabinoside	+	+	—
Q 3-0 diglucoside	+	+	+
Q 3-0 rhamnoglucoside	+	+	+
Q 7-0 glucoside	+	+	—

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8 Acknowledgment. This investigation was supported in part by the NRC of Canada, Grant No. A6663.

The Role of Glycine in the Biosynthesis of Steroids[1]

We have previously reported[1] that [2-^{14}C] glycine, [3-^{14}C] serine, [S-methyl-^{14}C] methionine, [^{14}C] formate and other progenitors of 'one-carbon units' can act as efficient substrates for the fungus *Cochiobolus miyabeanus* to produce radioactive ophiobolin B – a sesterterpene which can be derived from mevalonic acid. Interestingly, [1-^{14}C] glycine led to poor incorporation of radioactivity indicating that deamination of glycine to acetic acid did not occur to any appreciable extent. We believe that [3-^{14}C] pyruvic acid or equivalent is an intermediate in the biosynthetic pathway[1].

We report in the Table our observations on the biosynthesis of isoprenoids by *Saccharomyces cerevisiae*[2] in presence of labeled amino acids. Since the side chain of ergosterol carries an 'extra' methyl group known to be derived from one carbon donors such as methionine, it is essential to discount the radioactivity carried by this methyl group in evaluating the incorporation of radioactivity. Ergosterol from yeast purified by preparative TLC was subjected to slow oxidation with concentrated nitric acid; an aromatic acid-1-methyl-2, 3, 5, 6-tetracarboxy-

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