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Chapter 2

CHEMICAL ECOLOGY OF BRACKEN FERNS

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ABSTRACT

Ferns are among the oldest vascular plant lineages with origins dating back to the Devonian period. Bracken (*Pteridium* sp., Dennstaedtiaceae) is one of the most widespread and invasive fern species known to cause various ecological, economic and social concerns worldwide. This chapter highlights the important aspects of Bracken chemical ecology including its distribution pattern, interactions and defense. The chapter starts with the description of the global distribution pattern of Bracken delineating its ubiquitous nature followed by its

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interplay with abiotic factors such as soil-nutrients and fire. Further, interactions of Brackens with insects, microbes, plants and humans are discussed in detail. Various direct and indirect defense mechanisms employed by Brackens to deter pathogens and herbivores are reviewed. Brackens' chemical defense, especially norsesquiterpenoid glycoside 'ptaquiloside' is discussed in detail from its discovery and isolation to its reactivity towards biomolecules and potential impact on human health. The chapter concludes by raising a few fundamental research questions and resolving them which might help in understanding the ecological and evolutionary success of the plant.

1. Introduction

Bracken (*Pteridum* sp., Dennstaedtiaceae) is a cosmopolitan species and inhabits a wide range of habitats all around the globe. It is considered to be one of the most robust and invasive plants on earth. It can thrive in diverse ecological conditions from highly acidic to slightly basic soils (Marrs and Watt 2006); medium to high nutrient soils (Waring and Major 1964), slightly shady to open landscapes and extremes of temperature ranges except those in Antarctica where frost might be lethal. Several attributes of Brackens help in its colonization. For example, a long living, robust rhizome system which can resist high degrees of mechanical, herbicidal or biological control (Duc et al., 2003), high tolerance against a wide range of ecological conditions (Page 1986), high productivity which leads to large accumulations of litter, ability to produce shade providing frond canopy (Marrs et al., 2000), morphological plasticity, resistance against insect and pathogen attack, allelopathic effects on other plants (Gliessman 1976) and resistance to fire.

In comparison to other ferns, Brackens produce an unusually large number of toxic secondary metabolites like terpene glycosides, indanones and their glycosides, phenolics, flavonoids, phytoecdysteroids, tannins, lignins, silicates etc, among which terpene glycosides have been widely investigated to be toxic to mammals (Cooper-Driver 1976; Jones and Firn 1978; Schreiner et al., 1984; Tempel 1981). Interestingly, despite an arsenal of toxic chemical compounds, Brackens are associated with wide variety of insects (Cooper-Driver 1990; Cooper-Driver 1978; Marrs and Watt 2006), parasites and pathogens (Marrs and Watt 2006). This chapter describes the distribution and chemical ecology of Brackens aiming to provide insights into understanding the success of this fascinating plant across the world.

2. BRACKEN DISTRIBUTION

The macrofossil record of Bracken extends back to Oligocene, Miocene and Pliocene deposits in Europe and Australia (Page 1976). It is well distributed globally except in extremely cold environments like in Antarctica. Studies on the distribution of Bracken in Europe show that *Pteridium* is present throughout the whole continent. It can be found from the mountains in the south to Alps (*e.* 1800 m), Scandinavia, Urals and Finland in the north. In Italy, it is present from sea level up to 2100 m. The ecology of Bracken is well characterized in Britain (Marrs and Watt 2006), and recorded distribution limits range from sea level to an altitude of 600 m. To the west of Europe, the presence of Bracken is reported in the North Atlantic Islands, where in the Azores it is common in undisturbed soils (Ward 1970). In the Canary Islands, it is found in up to 1500 m (Page 1976). The presence of Bracken is also documented in Africa where it ascends beyond 3000 m mainly in the subalpine shrub zone of Kilimajaro (East Africa). It colonizes regions of forests around 2700 - 3000 m on Mt Kenya and the Imatong Mountains of Sudan at elevations, 1500 - 2500 m (Chipp 1929). Towards the west, it occurs both at sea level and open areas of higher elevations, colonizing areas of the Liberian coast (Harley 1955). In the south, Bracken is reported mainly on grassy areas, steep sunny slopes and in open shrub ground (Page 1976).

In Asia, *Pteridium* is presently abundant in the Himalayan region, Taiwan, and Sri Lanka, encompassing Thailand, Malaysia, Philippines, Java, Sumatra, Borneo and New Guinea, Japan, Hainan and Szechuan (Tryon 1941). It is also reported from 700 to 3300 m in India and up to 2500 m in China. It occurs throughout the Soviet Union, through Ladoga-

Il'men, Upper Volga, Volga-Kamon provinces, Western and Eastern Transcaucasia and Talysh, Southern Kuriles, Siberian-Mongolian frontiers, Ob region of Western Siberia and Yenisei of Eastern Siberia to Sakhalin, and Kamchatka (Page 1976). In the Cameron highlands of Malaya, reports document its presence to nearly 1700 m. It is present throughout the islands of the Philippines, to altitudes of ~ 2000 m (Copeland 1958; Page 1976). It is also commonly found in the temperate deciduous forests of Japan (Sleep 1970).

Bracken is widely distributed in North America from Alaska, Manitoulin Island, Alberta and Manitoba in the north to Florida and Mexico in the south (Page 1976). It extends from sea level in the Pacific north-west to nearly 3250 m in Colorado. The population of Brackens is abundant in the Washington-Oregon region and in the Douglas fir regions to the west of the Cascade Mountains. Phillip (1947) reported its presence from 1500 m to 2500 m in the Western Yellow Pine forests of Arizona. In Texas, it is mostly restricted to higher altitudes, ranging from 2150 to 2500 m. Further in Central America, *Pteridium* has been documented in Guatemala and Honduras up to 2800 m and from 1000 to 1300 m in the Revillagigedo Islands (Tryon 1941). It is widely distributed from *e*. 300-3000 m throughout the Hawaiian Islands. Some researchers have reported the presence of Bracken even around the volcanic craters of Oahu, Haleakala and Lesser Antilles (Page 1976). *Pteridium* has also been documentedin other island regions of the North American continent like Bermuda, Cuba, Jamaica, and the Galapagos. In South America, it has been documented in the District of Colombia up to ~ 3000 m in Venezuela, from 400-3000 m in Peru and Trinidad. However, species of *Pteridium* are relatively less abundant in South America when compared to other continents (Page 1976).

Pteridium is widely reported from all the states of Australia (Beadle et al., 1962; Page 1976) across Polynesia and Micronesia. In New Zealand, it extends from sea level to 1250 m in both North and South Islands like Stewart Island, and from the Kermadec islands to Auckland, Campbell Islands and Lord Howe Island. It is documented in the open dry woodlands of New Caledonia and the Solomon Islands (Page 1976).

2.1. Bracken Soil-Nutrient Dynamics

Bracken grows abundantly in diverse habitats and ecological conditions. It is found mostly on the open hillsides, scrubs, abandoned lands, forest clearings, burnt lands and edges of the thick canopy forests with mild, moist climates and abundant light, occasionally present in wet, marshy habitats. In open landscapes, plants are usually small and yellowish, whereas, they are large, bright green and less pubescent in shady conditions (Page 1976). It is the only fern reported in the sandy soils of pine plains (McFarland 1916). Typically, it grows well in deep, well drained, loamy, acidic soils. Maximum Bracken coverage is on fields with low fertility sandy/clay soils that had been previously used for growing crops and pasture (Suazo-Ortuño et al., 2015). Fertile alluvial soil fields, which were never used for pasture, had no Bracken. Several reports claim that Brackens thrive in pH ranging from highly acidic (pH ~ 2.8) to slightly basic (pH ~ 8.6) (Marrs and Watt 2006). Rainfall has a positive influence on Bracken growth whereas low temperatures influence it negatively (Portela et al., 2009). Brackens are extremely sensitive to frost and even the slightest contact with frost could be lethal. They are reported in varied environmental conditions ranging from coastal to sub-alpine regions (Brownsey and Smith-Dodsworth 1989). Its presence is even documented on schistose siliceous soils (Brownsey and Jermy 1973).

Brackens generally prefer soil with medium to high nutrient content (Ader 1990; Waring and Major 1964). Page identified 85 pteridophyte genera having the ability to grow on low nutrient substrates as ancient living vascular plants (ALVP) and *Pteridium* is one of them (Page 2004). Generally, Bracken improves soil fertility (Marrs et al., 1992) by either facilitating soil drainage or production of mull humus in the soil (Miles 1985). Literature suggests that Brackens influence edaphic processes like nitrification and increases mineralizable nitrogen (N) and ammonium (NH_4^+) ions in the soil (Marrs et al., 1992; Mitchell et al., 1997). A similar study by Soulsby and Reynolds (1994) on the relative contribution of deciduous trees, woody shrubs and *Pteridium* to soil nutrient deposition also suggested that N deposition rates are higher in soils inhabited by

Pteridium (Soulsby and Reynolds 1994). On the contrary, Brackens could lead to a decrease in soil N concentration and may enhance inorganic N-leaching to water streams (Smart et al., 2005). The same group reported higher C:N ratios in Bracken soils as compared to the grassland soils in 2007. They also noted increased ammonium concentrations in lower soil horizons as compared to upper soil horizons (Smart et al., 2007). Similarily, Bracken soils have lower potassium K^+, NO_3^-, NH_4^+ion concentration and denitrification enzyme activity rates in comparison to soils in the coniferous forests (Griffiths and Filan 2007). This led to the hypothesis that either N ions are leaching through the soil or Brackens have the ability to sequester soil N. However, the inconsistency in the studies on nitrogen dynamics in *Pteridium* soils might be partially due to the seasonal variations in soil processes (mineralization and uptake) and partly due to the methods used for assessing N turnover (Schimel and Bennett 2004). Later, DeLuca et al., (2013), integrated seasonal influences with multiple methods to assess N turnover in Bracken soils and soils under *Calluna vulgaris* (L.) and confirmed that Bracken promotes an open nitrogen cycle in heathland soils, wherein it leads to greater net nitrification and accumulation of nitrate (NO_3^-) in the soil (DeLuca et al., 2013).

2.2. Bracken and Fire

Bracken establishes in areas dominated by frequent fires, deforestation, agricultural activities like land clearing and burning, thus, causing serious concerns for farmers, foresters and conservationists (Pakeman et al., 1996). Fire plays a significant role in Bracken invasion and colonization as it had been frequently reported from burnt lands and fire prone areas (Cronquist et al., 1972; Tryon 1941). The invasive nature of Bracken has posed serious threats worldwide, like impeding the development of secondary forests, reduction in the quantity and quality of agricultural and grazing land, abandonment of farming land, loss of biodiversity and contamination of land and groundwater (Schneider and Geoghegan 2006). Brackens can form large colonies and impenetrable masses after fire. It is speculated that fire leads to conditions such as elimination of competitors, creation of sterile, alkaline and nutrient rich substrate, which are required for Bracken establishment (Page 1976, 1986). Trejo et al., 2010 evaluated the effect of fire-inducing temperatures on the viability of *Pteridium* spores. Their results suggested that spores buried a few centimeters below the soil have high percentage viability, which might give *Pteridium* a competitive advantage over other species, thus, leading to rapid establishment in burnt fields. Mapping the extent of Bracken infestation is of wide importance in order to formulate the restoration strategies for the invaded area.

3. Biotic Factors: Interaction with Insects, Pathogens, Plants and Humans

The evolutionary and ecological success of Bracken could be deciphered from its global distribution. While morphological plasticity could partly explain Bracken success globally, effective defense against herbivores, pathogens and competitors confers an enormous advantage in the evolutionary arms race. Francis Darwin wrote in 1876 “Bracken is singularly free from enemies not being eaten by the larger animals, by rodents or by grasshoppers” (Darwin 1876). Brackens interact with insects from primarily three groups, Hemiptera, Diptera and Lepidoptera. Literature suggests that spatio-temporal factors play a major role in determining the type and number of insects associated with Brackens. For example, researchers observed that *Macrosiphum ptericolens*, commonly known as Bracken aphid, is rarely associated with Brackens in summer (Marrs and Watt 2006). However, the population size increases dramatically from mid August until September. The cosmopolitan and robust nature of Bracken is well established, however, not all insects might have a wide survival range like Bracken. Therefore, this may be one of the plausible factors responsible for the observed correlation between the bio-geographical location of Bracken and the type of insect assemblages.

Insects found associated with *Pteridium* are both specialists and non-specialists (Cooper-Driver 1978; Lawton 1976; Marrs and Watt 2006). Table 1 gives the list of insects commonly known to be associated with Bracken.

Table 1. Bracken associated insects

Order	Family	Species	References
Coleoptera	Cerambycidae	*Sybra* sp.; *Tmesisternus* sp.	(Balick et al., 1978; Kirk 1978)
	Chrysomelidae	*Apthona* sp.; *Manobia* sp.	
	Curculionidae	*Baris atropolita; Strophosmos* sp.	(Balick et al., 1978; Kirk 1978; Wieczorek 1973)
	Elateridae	*Dalopius marginatus*	(Balick et al., 1978; Lawton 1976)
	Eucnemidae	*Dirhagus pygmaeus*	
	Helodidae	*Cyphon padi, C. variabilis*	
	Lathrididae	*Cartodere ruficollis*	
	Scarabaeidae	*Phyllopertha horticola*	(Balick et al., 1978; Lawton 1976; Wieczorek 1973)
	Scolitidae	*Poecilips pteridophytae*	(Balick et al., 1978)
Collembola	Bourletiellidae	*Bourletiella viridescens*	(Balick et al., 1978; Lawton 1976; Marrs and Watt 2006)
	Dicyrtomidae	*Dicyrtoma* sp.	(Balick et al., 1978; Lawton 1976)
Diptera	Agromizidae	*Phytoliriomyza hilarella, P. pteridii*	(Balick et al., 1978; Lawton 1976; Marrs and Watt 2006)
	Anthomyiidae	*Chirosia albifrons, C. albitarsis, C. histricina, C. parvicornis, C. betuleti, C. erassiseta, C. flavipennis; Pycnoglossa* sp.	(Balick et al., 1978; Cody and Crompton 1975; Lawton 1976; Marrs and Watt 2006; Wieczorek 1973)
	Cecidomyiidae	*Dasineura filicina, D. pteridicola, D. notha*	(Balick et al., 1978; Kirk 1978; Lawton 1976; Marrs and Watt 2006; Wieczorek 1973)
	Nabidae	*Jalla dumosa*	(Balick et al., 1978)
	Tingidae	*Corythucha padi*	
Hemiptera	Aphididae	*Macrosiphum ptericolens, M. pteridis; Idiopterus nephrelepidis; Shinjia pteridifoliae; Aphis pteris-aquilinoides, A. fabae; Mastopoda pteridis*	(Balick et al., 1978; Ghosh 1974; Lawton 1976; Marrs and Watt 2006; Patch 1938; Sorin 1962)
	Aphrophoridae	*Philaenus spumarius*	(Balick et al., 1978; Lawton 1976; Marrs and Watt 2006; Wieczorek 1973)
	Cicadellidae	*Calladonus commissus; Friscanus intricatus*	(Balick et al., 1978; DeLong 1948)
	Delphacidae	*Ditropis pteridis; Criomorphus*	(Balick et al., 1978; Lawton

Order	Family	Species	References
		pteridis	1976; Marrs and Watt 2006)
	Eriococcidae	*Eriococcus insignis*	(Balick et al., 1978; Hoy 1963)
	Miridae	*Bryocoris pteridis; Deraeocoris (=Camptobrochis) lutescens; Dicyphus globulifer; Lygus indistinctus; Macrolophus nubilus, M. punctipennis; Stenodema holsatum; Monalocoris filicis*	(Balick et al., 1978; Lawton 1976; Linnavuori 1975; Marrs and Watt 2006; Wieczorek 1973)
Hymeno-ptera	Tenthredinidae	*Aneugmenus furstenbergensis, A. padi, A. temporalis, A. coronatus, A. flaviceps, A. stamineipes, A.* sp.; *Stromboceros delicatulus; Selandria* sp.; *Embria* sp.; *Heptamelus ochroleucus; Empria excisa; Strongylogaster lineata, S. contigua, S. distans, S. filicis, S. maculata, S. mixata, S. multicinctus, S. tibialis, S. xanthoceros, S.* sp., *S. multifasciata*; *Tenthredo ferruginea, T. colon, T. balteata, T. livida, T.* sp.	(Balick et al., 1978; Beer 1955; Cody and Crompton 1975; Hogh 1966; Lawton 1976; Marrs and Watt 2006; Ross 1932; Van Leeuwen 1938; Wieczorek 1973; Venkatesan et al., 2012)
Lepido-ptera	Tortricidae	*Olethreutes lacunana*	(Marrs and Watt 2006)
	Arctiidae	*Arctia caja; Diacrisia pteridis; Spilosoma luteum*	(Balick et al., 1978; Lawton 1976; Tietz and Tietz 1972)
	Gelechiidae	*Paltodora cytisella; Depressaria impurella*	(Balick et al., 1978; Lawton 1976; Marrs and Watt 2006; Wieczorek 1973)
	Geometridae	*Idiodes apicata; Campaea ada, C. biplaga; Hemichloreis exoterica; Homochlodes lactispargaria, H. fritillaria, H.* sp.; *Petrophora chlorosata, P.* sp.	(Balick et al., 1978; Common 1990; Lawton 1976; Marrs and Watt 2006; Wieczorek 1973)
	Hepialidae	*Hepialus fusconebulosus, H. hectus, H. sylvinus*	(Balick et al., 1978; Lawton 1976)
	Limacodidae	*Hedraea quadridens*	(Common 1990)
	Noctuidae	*Ceramica pisi; Phlogophera meticulosa; Callopistria cordata, C. granitosa, C. mollissima, C. juventina, C. latreilli, C. purpureofasciata; Euplexia benesimilis, E. lucipara; Habrynthis (= Phlogophora) scita; Laconobia (= Mamestra) contiqua, L. oleracea; Papaipema pterisii; Peridroma margaritosa; Phlogophora meticulosa; Polia adjuncta, P. assimilis*	(Balick et al., 1978; Common 1990; Essig 1958; Lawton 1976; Marrs and Watt 2006; Tietz and Tietz 1972; Wieczorek 1973)

Table 1. (Continued)

Order	Family	Species	References
	Pyralidae	*Psara platyeapna*	(Balick et al., 1978; Kirk 1978)
	Tineidae	*Praecedes theeophora*	
	Tortricidae	*Epiphyas postvittana*	(Common 1990)
Sarcopti-formes	Chamobatidae	*Chamobates* sp.	(Balick et al., 1978; Lawton 1976)
Trombidi-formes	Eriophyidae	*Eriophes pterides; Phyllocoptes dimorphus*	(Balick et al., 1978; Kiefer 1940; Van Leeuwen 1938)

Further, a variety of arthropods, pathogens and parasites had been found to be associated with Bracken. For example, Bracken spores, prothalli and rhizoids are consumed by some species of Collembola like *Isotoma viridis* and *Lepidocyrtus cyaneus*. Some algal pathogens such as *Chlamydomonas* sp., *Chlorella* sp., *Protococcus* sp. and *Stichococcus bacillaris* are known to feed on Bracken (Conway 1949). A total of 26 species of fungi have been recorded from Bracken fronds including *Tilachlidium* sp. Preuss. (Ascomycota: Hypocreales), *Pythium* sp. Pringsh. (Oomycota, Pythiaceae), *Coniothyrium* sp. Corda. (Ascomycota: Leptosphaeria), *Corticium anceps* (Bres. & Syd.) Gregor (Basidiomycota, Corticiaceae), *Botrytis cinerea* Pers. (Ascomycota, Sclerotiniaceae), and leaf spot *Ascochyta pteridis* Bres. (Ascomycota, Didymellaceae) (Hutchinson and Fahim 1958; Marrs and Watt 2006). In the same study, *Aureobasidium pullulans* (de Bary) Arnaud (Ascomycota, Dothioraceae), *Phoma* sp., *Cylindrocarpon destructans* (Zinssm.) Scholten (Ascomycota, Nectriaceae) and *Stagonospora* sp. are reported as endophytes of Bracken (Marrs and Watt 2006). Given these associations with a variety of biotic agents, combined with the immense ecological success of Brackens around the globe leads to the question, how does *Pteridium* deal with natural enemies?

3.1. Chemical Defenses of Bracken

Bracken harbors a large variety of secondary metabolites, which could play a role in its defense (Cooper-Driver 1976; Jones and Firn 1978;

Schreiner et al., 1984; Tempel 1981). A number of these compounds are known to play an important role in Brackens' defense against insects and pathogens. For example, Schreiner et al., (1984), reported a significantly lower number of insects, reduced larval growth and higher larval mortality on cyanogenic fronds. Avila-Núñez et al., (2008), observed that *Bolax palliata* prefers to attack *Pteridium* sp. with a higher concentration of condensed tannins. In this case, the preference could be due to sequestration by the beetles. Bracken also contains other toxic compounds like caffeic acid and quercetin which have been shown to be detrimental for the growth of greenbug, *Schizaphi graminum* (Todd et al., 1971). Ecdysones are steroidal hormones, which regulate developmental transitions in insects like larval molting and metamorphosis. Phytoecdysteroids are synthesized by plants as a defense against phytophagous insects, conferring immunity against predators. Jones and Firn (1978), reported that four species of insects (*Pieris brassicae*, *Chilopartellus*, *Phyllobius pyri*, *Phyllobus argentatus*) were deterred by Bracken ecdysteroids at concentrations >60 mg/kg FW but this had no effect on *Schistoeerca gregaria* and *Spodoptera littoralis* even at higher concentrations. This could be either because these insects possess a mechanism to detoxify these compounds or the ineffectiveness of a toxic metabolite singularly. Especially since plants rarely rely on a single metabolite for defense, one could speculate that some of these metabolites act more efficiently as mixtures. Given the paucity of studies on plant-derived ecdysones in general, the role of Bracken ecdysones warrants further investigation.

The concentrations of chemical compounds from Bracken show spatio-temporal variations and differ significantly with age of the plant and between ecotypes. Seasonal variations were observed in the concentrations tannins, lignin, silicates and pro-anthocyanins (Lawton 1976). Brackens growing in shade contain lower quantities of tannins while higher concentrations of thiaminase and cyanogenic glucosides are reported in young fronds, in early season that declined as the season progressed (Cooper-Driver et al., 1977; Lawton 1976). Such spatio-temporal variations also influence insect and pathogen interaction with Brackens, e.g., graminivorous *Locusta migratoria* and *Schistocerca gregaria* rarely feed on Bracken fronds late in the season (Carlisle and Ellis 1968).

3.1.1. Discovery of Ptaquiloside: 'Cattle Poisoning' to 'Carcinogenicity'

The toxicity of Bracken on cattle has been suspected from time to time since the last decades of nineteenth century. A veterinary researcher from Great Britain presented significant experimental evidence to support 'cattle Bracken poisoning' (acute pyrexia, multi-organ haemorrhages leading to death) on bull-calf upon ingestion of fronds through a period of twenty-five days (Stockman 1917). Another study by the same author in 1922 provided definite evidence to exclude the scope of avitaminosis causing cattle illness and concluded the Bracken to be a poisonous plant (Stockman 1922). Later, multiple studies by Evans et al., unequivocally established Bracken poisoning through symptotic expression of bone-marrow aplasia including leucopenia, thrombocytopenia and haemorrhages in ruminants (Evans et al., 1954a,b, 1958, 1959). They also firmly eliminated the possibility of avitaminosis B_1 in cattle due to the presence of thiaminase in Bracken. Its carcinogenicity was reported for the first time by Rosenberger in 1960 (Rosenberger and Heeschen 1960). Evans et al., (Evans and Mason 1965) documented the development of multiple adenocarcinomas protruding into the small intestine (ileal region) of rats ingested on Bracken rich diet for a long period thereby establishing the carcinogenicity of this edible fern. Successive studies in the next few years also supported this finding (Hirono et al., 1970; Pamukcu and Price 1969; Price and Pamukcu 1968). It attracted more attention when scientists found the toxin and carcinogen (s) are capable of being transported through the milk of cows fed on Bracken. Consequently, identification and characterization of carcinogen(s) present in the Bracken became essential from the perspective of veterinary science and human health. Unfortunately, due to the probable instability of the carcinogenic metabolite and lack of efficient bioassay, isolation of the carcinogen remained unattained for a long time. In 1983 Yamada et al., successfully isolated and structurally characterized an illudane type norsesquiterpene glucoside from Bracken named ptaquiloside (1) (Niwa et al., 1983a, et al.,b). 1 was proven to be the ultimate carcinogen from Bracken by the same research group through feeding tests of the fractions and purified ptaquiloside on rats (Hirono et al., 1984b). Subsequently, in a study by the same group in 1987, a batch of female ACI rats, when fed on a diet containing 1 (0.027-0.08%) for a period of 210 days developed ileal (adenomas and adenocarcinomas) and urinary tumors (Hirono et al., 1987). Another study also showed that the symptoms of acute Bracken poisoning can be induced by 1 in cattle (Hirono et al., 1984a).

3.1.2. Properties of Ptaquiloside; Solubility, Stability and Reactivity

1 is highly soluble in water with a logarithmic partition coefficient in octanol-water and ethyl acetate-water being -0.63 and -0.88 respectively (Rasmussen et al., 2005). It has good solubility in ethyl acetate (partition ratio between water and ethyl acetate is ~6:1). In an aqueous solution, it gradually decomposes and the rate of decomposition depends upon the pH. In highly acidic pH (<4), ptaquiloside gradually loses its glycone moiety (D-glucose) and aromatizes to pterosin B (Figure 1). Saito et al., (1989) reported that at pH 4, the half-life of 1 is less than 7 days. At pH >8, it rapidly decomposes to pterosin B through an intermediate Bracken dienone (Figure 1). At pH 11.5 it completely converts into pterosin B within 20 min. The cyclopropyl ring at C-7 in Bracken dienone acts as an electrophile (through the formation of non-classical cyclopropyl carbocation), which is in extended conjugation with a ketone. Consequently, the Bracken dienone acts as a highly reactive alkylating agent towards nucleophiles such as water, alcohols or amines to furnish the stable aromatic skeleton of 1-indanone (Yamada et al., 2007). For example, cysteine, methionine, glutathione are alkylated by Bracken dienone in aqueous acetone to yield corresponding 1-indanone substituted sulphides along with the major product pterosin B. In case of nucleosides, alkylation occurs on the purine/ pyrimidine bases (<3%) where nucleotides undergo alkylation at the phosphate group (Ojika et al., 1987).

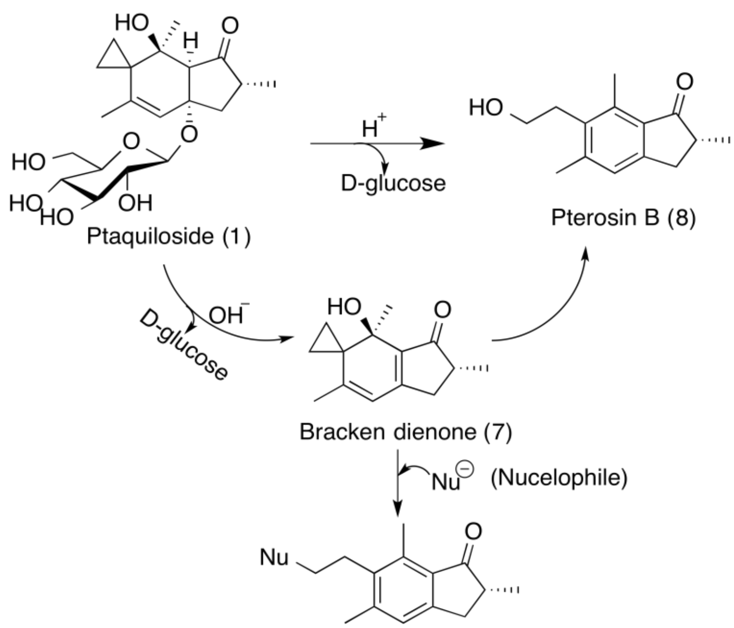

Figure 1. Decomposition of Ptaquiloside (1).

3.1.3. Carcinogenicity: Molecular Mechanism

Structural modification of DNA through covalent binding with genotoxins is a common cause of chemical carcinogenesis. Ojika et al. (1989), incubated salmon sperm DNA with dienone in an aqueous acetone solution (pH 7.5, 37°C) and analyzed the binding site on DNA through thermal hydrolysis. Two alkylated purine bases (N-7 alkylated guanine and N-3 alkylated adenine\) were isolated from the hydrolysed product. In 1994 the molecular mechanism of DNA- dienone interaction (Figure 2) and sequence preference were described (Kushida et al., 1994). The most favorable cleavage was reported to be at 5′-AAAT. DNA-dienone adduct was detected in ileum tissue of calves fed on Bracken through ^{32}P post-labelling assay and mutation on H-*ras* oncogene through single strand conformation polymorphism analysis (Prakash et al., 1996). They also observed the adenine specific alkylation on H-*ras* genes followed by a sequence selective rate of depurination *in vitro*. The potential of dienone (the activated form of ptaquiloside) as a carcinogen was thus established *in vivo* (Shahin et al., 1998).

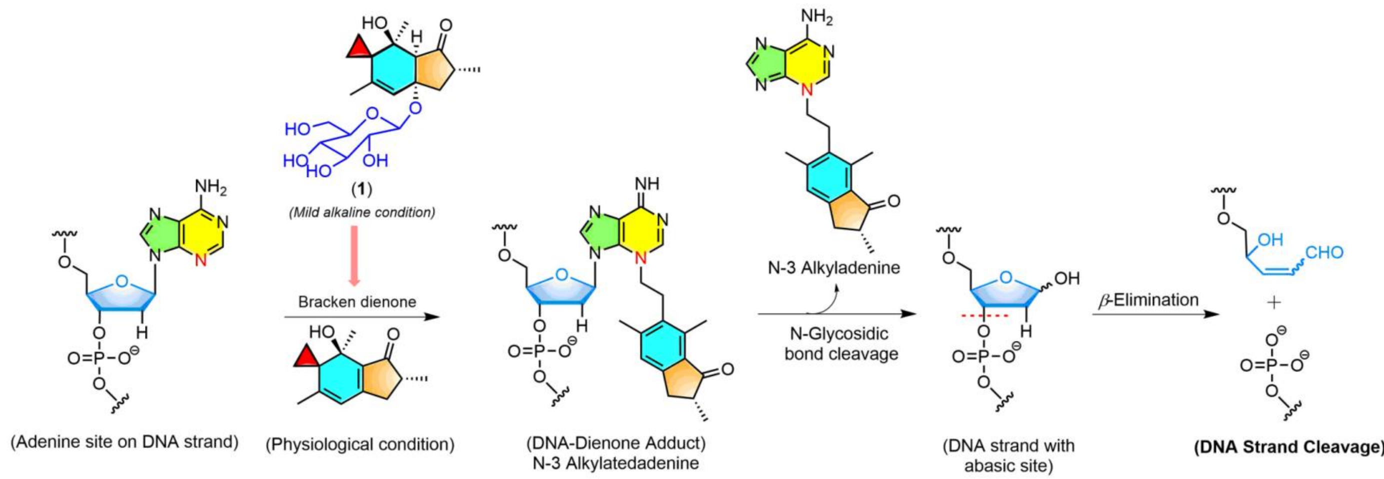

Figure 2. Molecular mechanism of DNA cleavage by Bracken dienone.

3.1.4. Isolation and Analysis of Ptaquiloside

The instability of 1 (especially towards pH) leading to the formation of pterosin B made its isolation challenging to chemists. After the first isolation, (Niwa et al., 1983a) several successive studies were published demonstrating improved isolation protocols with milder steps and better yields. In the original carcinogenicity-guided protocol, the hot water extract of dried Bracken powder was treated with the adsorbent resin, Amberlite XAD-2. The methanol eluate was further concentrated, partitioned, resin treated (Toyopearl HW-40) and subjected to multiple chromatographic steps to furnish 1 in 0.02% yield. Later, the same authors published a simpler protocol with a better yield (0.1%) where Bracken was extracted with water at room temperature (Ojika et al., 1985). The major modifications in the isolation method were made by Oelrich et al., (1995). According to their observation, (i) the majority of the loss happened during concentration in water at high temperature, (ii) 1 is less stable in aqueous solutions than methanol even at low temperatures, (iii) 1 is sensitive to light exposure. The isolation protocol was designed by careful elimination of these conditions. 1 was established to be the major causative agent for the toxicity and carcinogenicity induced by Bracken in livestock. Consequently, it became very important to develop efficient and sensitive analytical methods to detect and quantify 1 in various samples. The available methods to date can be divided into direct and indirect categories. In direct analysis, intact 1 in the sample is detected and quantified. In case of the indirect method, it is quantitatively converted into pterosin B (8) through base-acid treatment and is quantified as an indirect estimation of 1. Indirect analysis is helpful during the presence interfering compounds and eliminates the discrepancy due to the decomposition of 1 during sample preparation or chromatographic analysis. Table 2 describes the analytical methods for the estimation of 1 in natural samples.

Table 2. Chronological development of analytical methods for the analysis of ptaquiloside (1) and pterosin B (8) [LOD: Limit of Detection and LOQ: Limit of Quantification]

Year	Author	Technique	Sample Type	Sample preparation	Sensitivity
1991	(Agnew and Lauren 1991)	HPLC	Bracken tissue	Aqueous extraction, polyamide clean-up, base-acid treatment (for indirect detection)	LOD (mg/g): 30 (1), 5 (8)
1992	(Alonso-Amelot et al., 1992)	HPLC	Bracken tissue	Water extraction, base treatment, dichloromethane extraction, microcolumn pre-purification	0.1 µM
2008	(Jensen et al., 2008)	LC-MS/MS	Soil and ground water	*Soil*: 5 mM NH_4OAc extraction (1) followed by 80% aqueous methanol extraction (8) *Ground water*: Pre-concentration through SPE cartridge	LOD (µg/L): 0.19 (1), 0.15 (8)
2011	(Francesco et al., 2011)	GC-MS	Milk of farm animals	Carbograph adsorption, elution, NaBr treatment, diethyl ether extraction	LOQ (µg/L): 0.3 (Bromopterosin B)
2011	(Fletcher et al., 2011)	GC-MS and HPLC-UV	Bracken tissue	Aqueous extraction, polyamide clean-up, base-acid treatment	-
2014	(Aranha et al., 2014)	LC-MS	Cattle plasma, urine and milk	Pre-concentration through SPE cartridge	LOQ (ng/mL): Plasma: 1.2 (1), 3.7 (8) Urine: 52 (1), 33 (8) Milk: 5.8 (1), 5.3 (8)
2014	(Zaccone et al., 2014)	GC-MS	Bracken tissue and soil	Water extraction, NaBr treatment, diethyl ether extraction	LOQ (µg/L): 0.3 (Bromopterosin B)
2015	(Virgilio et al., 2015)	GC-MS	Milk of healthy farm animals	Carbograph adsorption, elution, NaBr treatment, diethyl ether extraction	LOQ (ng/mL): 0.4 (Bromopterosin B)
2016	(Clauson-Kaas et al., 2016)	UPLC-MS/MS	Preserved natural water	Pre-concentration through SPE cartridge	LOQ (µg/L): 0.44 (1), 0.25 (8)

3.1.5. Ptaquiloside: A Global Concern to Human Health

The abundance of potent carcinogen 1 in edible Bracken and its probable transportation to humans through direct consumption or vectors have raised concerns among scientists. In central Japan, the probability of oesophageal cancer increased in men and women by 2.1 and 3.7-fold respectively due to the consumption of Bracken (Warabi) (Hirayama 1979). In North Wales, UK the high cases of gastric cancer among the population was found to be related to Bracken intake (Galpin et al., 1990). In the AuroPreto area of Brazil, a retrospective case-control study showed patients ingesting Bracken shoot had a 5.47 times higher ‘chances ratio’ for upper digestive tract cancer (Marliere et al., 1998). Similar statistics were reported in Venezuela where the gastric cancer death rate was 3.64 times higher in Bracken populated highland areas (Alonso-Amelot and Avendano 2001). The abundance of 1 in the Bracken sample may vary over a wide range depending on the geographical location, type of fern tissue, collection season and species (Smith et al., 1994; Dawra et al., 2002). In multiple studies the abundance of 1 was found to be higher in young developing tissues such as croziers than fronds/rhizomes especially during spring and early summer (Alonso-Amelot et al., 1992; Rasmussen et al., 2003a). On the other hand, a dramatic variation can be observed in the levels of ptaquiloside through different Bracken varieties. In Venezuela, the amount of ptaquiloside in *P. caudatum* and *P. arachnoideum* was reported to be 1.98-3.90 mg and 0.03-0.66 mg/g of newly emerged crosiers (Alonso-Amelot et al., 1995). Evans and co-workers first reported the transport of Bracken toxicity through cow-milk in 1972 (Evans et al., 1972). It was further supported by Pamukcu et al., who proved that the milk of cows fed on Bracken is carcinogenic and caused tumours in mice (Pamukcu et al., 1978). Alonso-Amelot et al., detected ptaquiloside in milk for the first time (>11mg/L) (Alonso-Amelot et al., 1993, 1996). According to their calculation, a person consuming 0.5 L milk a day may intake 10 mg of ptaquiloside (assuming the cow ingested 6-7 kg Bracken a day). With the advancement of reliable and sensitive analytical techniques, 1 could be detected not only in fern-fed cattle but also in healthy farm animals such as cows, goats, sheep, donkeys and horses (0.4-1.9 ng/mL) from Southern Italy (Francesco et al., 2011). Further, 1 was up to 3.14 ng/mL in the raw milk of healthy sheep and goats grazing on Bracken abundant pasturelands in the same geographical location (Virgilio et al., 2015). The abundance of 1 (0.22-8.49 µg/g) was reported for the first time by Rasmussen et al., (2003) in soils under Bracken vegetation exposed to heavy showers just before sampling. According to their calculation, potentially 0.05-0.25% of total ptaquiloside content might be leached from the Bracken leaves. They also studied the sorption, degradation and mobility of ptaquiloside in soil to provide a better insight into soil contamination (Rasmussen et al., 2005). The rate of degradation was slow in less acid sandy soil with half-life of several days, especially in low temperatures (4°C). Conclusively, the degradation depends on the acidity, clay and carbon content of the soil and microbial activity. Recently, 1 was detected in 5 samples (among 21 samples) of the ground water below Bracken vegetation in Denmark and the level was up to 92 ng/L (Clauson-Kaas et al., 2014). These reports indicated a substantial risk of ptaquiloside intake by the local population through surface/ground water. Spores of Bracken constitute another route of contamination and can be potentially risky for the local people such as forestry workers in Bracken infested areas. In a study, 53 mice within a group of 98 dosed with Bracken spores developed tumours (Evans 1987). Further, in the upper gastrointestinal tract of spore administered mice, formation of DNA adducts were observed (Povey et al., 1996). However, transportation/contamination by spores might be only secondary when compared to milk or water (Rasmussen et al., 2013).

The toxicity and carcinogenicity of Bracken has captivated the interest of natural product chemists to explore the rich reserve of its secondary metabolites for a long time (Yamada et al., 2007). After the discovery of 1, several of its structural analogues have also been isolated and characterized from Bracken including isoptaquiloside, (2) (C-8 epimer), caudatoside, (3) (2α-hydroxymethylptaquiloside) (Castillo et al., 1997), ptaquiloside Z, (4) (2-methyl ptaquiloside) (Castillo et al., 1998), pteridanoside, (5) (proto-illudane skeleton) (Castillo et al., 1999) and ptesculentoside, (6) (10-hydroxy ptaquiloside) (Fletcher et al., 2010) (Figure 3, 1-6). They are considered to be the major group of carcinogens present in Bracken. A series of 1-indanones (pterosins) and their glycosides (pterosides) have been reported from Bracken rhizomes and fronds during 1970-80 (Fenwick 1989; Fukuoka et al., 1978; Mohammad et al., 2016).

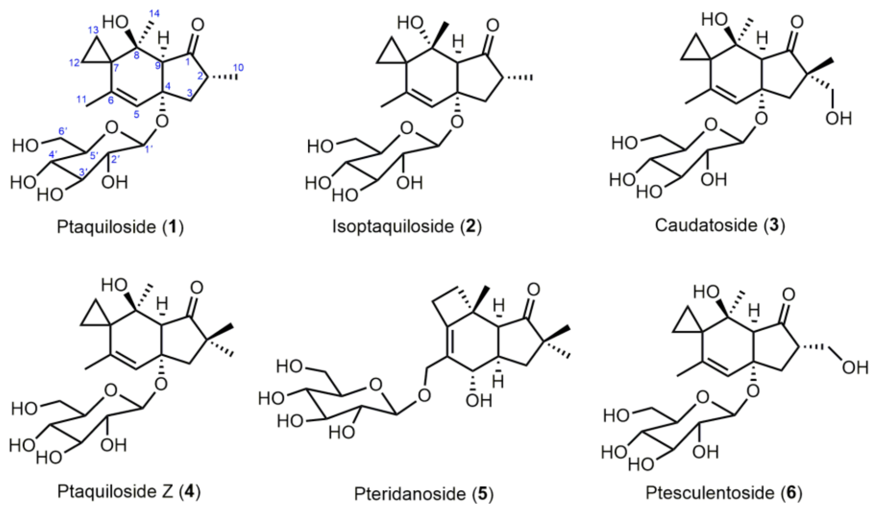

Figure 3. Illudane type glycosides from Bracken.

3.2. Indirect Defenses of Bracken

As a classic example of “the enemy of my enemy is a friend”, plants employ indirect defenses to attract, nourish and sometimes even house members of the third trophic level to cope with herbivores. By secretion of indirect defense rewards like extra-floral nectar (EFN), plants attract ants as bodyguards that show significant reduction in herbivory. Similarly, herbivore damage is known to induce a specific blend of Volatile Organic Compounds (VOCs) that serve as a cue to parasitoids and predatory insects. VOCs thus act as an indirect defense to protect the plant from herbivore damage. Several studies have established the role of indirect defenses in plants and their regulation by jasmonates (JA), the key phytohormones of the octadecanoid signaling pathway. However, comparatively, very less is known on lower plants such as Bracken. Bracken is one of the few ferns that harbor EF nectaries. Out of the 36 families in Pteridophytes (Smith et al., 2006), the presence of EFNs is reported in a total of 4 families, namely Polypodiaceae, Dryopteridaceae, Dennstaedtiaceae and Cyatheaceae. Studies on EFNs from ferns have demonstrated its importance in a plant's defense. For instance, Koptur et al., (1998), observed reduced plant herbivory in *Polypodium plebeium* due to association of ants with plant nectaries.

EFNs in Brackens are conspicuous structures present at the base of each pinna, sometimes at the base of pinnules as well (Figure. 4). These are dark brown, well defined structures composed of thin walled epidermis and secretary parenchyma cells, which differ significantly from vascular tissue composed largely of large parenchyma cells (Rumpf et al., 1994). Studies conducted in the northern hemisphere revealed that nectar secretion is greatest in mid-June and during the initial frond expansion process, this becomes zero in late August. Many different types of ants have been frequently reported to be associated with Bracken nectaries (Lawton and Heads 1984). Francis Darwin (1876) believed that the "primary role of nectaries in Bracken is as waste glands or excretory organs and the ants associated with Brackens play no role in plant defense mechanisms because Bracken has no natural enemies" (Darwin 1876). Since then, various research groups have been working to decipher the type of interaction between Brackens and ants and the potential role of nectaries in Bracken defense with little success.

Figure 4. Extra-floral nectaries of Bracken.

Studies on interactions between ants and Brackens mostly described ants to be commensals and opportunistic feeders (Cooper-Driver 1990). Tempel (1983) studied the role of ants in Bracken defense and observed no difference in the degree of herbivory on plants visited by ants. Later it was reported that ants could impose very high rates of predation on experimentally introduced caterpillars, which are non-adapted to Brackens as compared to insects that are immune to ant visits (Heads and Lawton 1985; Lawton and Heads 1984; Rashbrook et al., 1992). For instance, Bracken sawflies, *Strongylogaster*, *Aneugmenus* and *Tenthredo* hemolymph were found to be repellent to ants (Heads and Lawton 1985; Pasteels et al., 1983). This could be an adaptation strategy of specialized feeders of Bracken.

Although ant-nectary association is not directly involved in Bracken defense, ants might act as bodyguards for bracken. For example, two large ant species, *Formica* sp. and *Camponotus* sp. defend by biting, stinging or killing insects (Heads 1986). Furthermore, the presence of ants on Brackens correlate with the amount of nectar secretion. Tempel (1983) observed that ant activity was highest in fiddleheads, which secrete higher EFN. The first evidence that ants confer fitness benefits was provided by exclusion experiments. Sawfly egg abundance was significantly higher on fronds from which ants were excluded (Jones and Paine 2012). Thus, ant-plant interaction might provide indirect benefits to Bracken through decreased insect oviposition.

Emission of VOCs constitutes an indirect defense strategy employed by several plants. VOC emission has been shown to benefit plants by attraction of predators and parasitoids (Imbiscuso et al., 2009). While VOC emission and regulation is well characterized in higher plants (Hopke et al., 1994; Röse and Tumlinson 2004), very little is known in lower plants like the ferns. Imbiscuso et al., were the first to study VOC emission from the fern, *Pteris vittata* L. (Pteridaceae) upon attack by a generalist herbivore, *Spodoptera littoralis* (Imbiscuso et al., 2009). They found that some of the VOCs produced by *P. vittata* were similar to those detected in higher plants such as (*Z*)- ß-Farnesene, (*E*)- ß-farnesene, (*E*)- nerolidol, (*E*)-3-hexen-1-ol and benzaldehyde. Kessler et al., (2015) studied the VOC production in grammitid fern and analyzed dried specimens of six ferns. A total of 38 VOCs were detected, out of which 22 had not been previously reported in ferns (Kessler et al., 2015).

The first study on VOC emissions from Bracken upon herbivore damage was reported in 2012 (Venkatesan et al., 2012). The authors found that both generalist (*Spodoptera littoralis*) and specialist (*Strongylogaster multifasciata*) herbivore attacks lead to the induction of VOCs in Bracken, but the amount was low when compared to higher plants. The authors also studied VOC emission upon exogenous application of JA and its precursors, 12-oxo-phytodienoic acid (OPDA) and α- linolenic acid. Results indicated that treatment with JA led to significantly higher production of terpenoid volatiles as compared to those released upon insect damage. The endogenous level of JA after herbivore damage was also very low in Bracken when compared to higher plants. These results indicated a missing link between herbivory and JA-regulated VOC production in Bracken. Taken together, these studies suggest that more comprehensive studies on the types and quantity of volatiles released in ferns upon insect attack are needed to decipher the evolutionary origin and ancestral significance of these plant defense mechanisms.

3.3. Interaction with Other Plants (Allelopathy)

Allelopathy is a phenomenon by which an organism produces bio-chemicals that influences germination, survival, development and/or reproduction of other organisms (Cheng and Cheng 2015). Allelochemicals may influence other plants directly via phytotoxicity or indirectly by producing environmental modifications like interfering with soil microbiota and/or influencing the availability of soil nutrients. An understanding of Bracken interaction with other plants is of utmost importance, as it is known to be highly invasive (Cooper-Driver 1990). Extracts from Bracken in different media have been tested for their toxicity on different plants. Water-soluble extracts of Bracken fronds were shown to reduce the germination of western Thimbleberry and Salmonberry. This phytotoxic effect was attributed to the presence of cinnamic acid or benzoic acid derivatives (Bohm and Tryon 1967; Gliessman and Muller 1972). Reports suggest that *Pteridium* leachate has more pronounced effects on secondary species as compared to pioneer species of Bracken (Silva-Matos and Belinato 2010). The alcoholic extract of *Pteridium* was found to inhibit the germination, growth and development of *Poa pratensis* seedlings. This was attributed to the presence of sesquiterpenoids, pterosin B and pterosin F in the alcoholic extract of Brackens, both of which are inhibitory to seed germination and development (Butnariu et al., 2015). Similarly, reduction in the radicle length of Douglas Fir was documented in the presence of Bracken litter extracts (Moral and Cates 1971). This was correlated with other field studies, which noted the reduced height of Douglas fir seedlings on sites dominated by western Brackens (Dimock 1964). Recently, Jotaba et al., isolated an allelochemical, Selligueain A from Bracken (fronds and litter) and from the soil below the Bracken patch in the Tropical Savanna reserve area in Brazil (De Jatoba et al., 2016). It was shown to possess the phytotoxic activity against the early development of *Sesame indicum*, further validating the allelopathic potential of *Pteridium* and explaining its dominance (De Jatoba et al., 2016).

CONCLUSION

Robustness, multi-layer defense and allelopathic potential has caused Bracken to be ubiquitous, invasive and ecologically successful since the early era of plant evolution. Therefore, Bracken owns a distinct place in the plant kingdom and needs to be investigated further to answer fundamental unknowns in plant evolution such as how did ancient plants defend themselves against insect herbivores? Does JA/SA regulated defense mechanisms operate in lower plants as well? What is the role of EFN and VOCs in ferns? Given that ferns are early diverging euphyllophytes, a better understanding of their chemical ecology may provide novel insights into plant defense mechanisms as well as provide a unique opportunity to investigate gametophyte-specific interactions. Ferns hold evolutionarily critical position as being the most closely related extant land plant lineage to seed bearing plants and yet we remain limited in knowledge, about many aspects of their chemistry and ecology. Two fern species, *Ceratopteris richardii* and *Azolla sp.* are currently emerging as model systems for ferns and efforts are underway to sequence their genomes that would be valuable for fern research.

On the other hand, a major Bracken toxin and carcinogen, ptaquiloside is a glucosidated member of illudin- type nor- sesquiterpenoids, which are rarely found in nature. An abundance of this class of molecules is mainly confined to toxic *Omphalotus* mushrooms (e.g., bioluminescent mushroom Jack-o′-Lantern) (McMorris and Anchel 1965; McMorris et al., 1992) whereas ptaquiloside is exclusively produced by ferns. While ptaquiloside is toxic and carcinogenic to mammals, there are insects which survive on Bracken avoiding the toxicity. It will be of great importance to understand the molecular mechanism of toxin (ptaquiloside) adaptation by the insects that feed on Bracken. As Bracken invasion is a major issue and disrupts the ecological balance around the world, development of effective bio-control agents will be highly demanding in the field of forestry and veterinary science. In regards to food safety and human health, detoxification or ways to avoid the contamination of ptaquiloside in consumables has to be established, especially in Bracken-infested areas. Also, the massive biomass of this highly populated fern is mostly unused until today and might have a potential for value-added products in industry. Overall, it is an exciting time for studying ferns as many more novel insights about fundamental processes in plants could be discovered. Taken together, Bracken is a fascinating plant that has to be studied for its unique chemistry and general ecological success. There is lot more to be learned from this fern in terms of plant defense and its regulation by plant hormones. In essence, Bracken can be of immense interest to researchers from different arenas of science and technology in near future.

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