Phytochemistry of Indian Pteridophytes: A Review

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Abstract

In the present review, an attempt is made to provide an update on the phytochemistry of Indian pteridophytes, covering the recent findings concerning the phytochemical composition of crude extracts and their histochemical, spectroscopic and chromatographic profiles. Primary and secondary metabolites of Indian pteridophytes qualitative and quantitative profiles are taken into consideration. A report on the preliminary phytochemical analysis of 170 species, primary and secondary metabolites quantitative profiles of 115 species, histochemical profiles of 61 species, chromatographic profile (amino acids and sugar) of 43 species, TLC profile of 14 species, HPLC and HPTLC profiles of 23 species and GC-MS profiles of 32 species is included for the present review. The results confirmed the existence of the secondary metabolites, viz. phenolics, tannins, flavonoids, steroids, saponins, triterpenoids, glycosides and alkaloids, in the Indian pteridophytes. The available literature on phytochemistry confirmed that Indian pteridophytes are a pool of therapeutic agents. The outcome of the preliminary phytochemical studies on the qualitative and quantitative profiles of Indian pteridophytes revealed the chemical constituents and therapeutic values and

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provided the chemical marker for the studied pteridophytes. These profiles will be used as phytochemical markers for the identification of the species in the pharmaceutical industries and to find a solution for the taxonomical disputes. Further studies on the isolation and characterization of active principles responsible for the bioactivity are needed.

Keywords

Chromatography · Histochemistry · Metabolites · Spectroscopy · Ferns · Fern allies

19.1 Introduction

Pteridophytes (ferns and fern allies) are the primitive vascular plants that appeared on the earth in the mid-Paleozoic Era. They are the pioneer colonizers on earth and one of the ubiquitous vegetation that dominated the land in the Carboniferous period. Pteridophytes with their specialized water and food- conducting tissues heralded an era of great colonization in terrestrial ecosystems. They successfully established themselves as land plants and dominated most of the forests on earth's surface. It was a very rapid rate of evolution. It possesses simple organization and is unique in being characterized by cryptogamic mode of reproduction. They are very conspicuous and gorgeous elements of biodiversity which occurs in various kinds of habitats ranging from sea level to mountain top and tropical to subpolar regions (Dudani and Ramachandra 2010). The decline of pteridophytes began with the evolution and dominance of the flowering plants in the late Cretaceous. Since then, pteridophytes act as a bridge between the non-vascular cryptogams and the phanerogams. It continues to occupy several niches on the land, in marshes and even in water bodies (Dudani et al. 2011).

Pteridophytes represent a broad spectrum of biological types from small filmy to arborescent tree ferns and from submerged aquatics to epiphytes and xerophytes (Kumar 1998). They are very conspicuous and elegant elements of our present- day flora. They had a very glorious past being the dominant vegetation on the earth about 280–230 million years ago (Bir 1987; Khare 1996). They are the beautiful elements of biodiversity and occur in a wide range of habitats from sea level to mountain top and tropical to subpolar regions. Pteridophytes attracted the attention of botanists because of their characteristic life cycle in which the sporophytic and gametophytic generations not only are independent to each other but also are usually autotrophic and morphologically distinct. They are the wonderful group of plants with fascinating foliage architecture and have drawn special attention of the plant lovers, researchers and horticulturists. In the world flora, about 13,600 species of extant pteridophytes are recorded (Moran 2008). Among which 1300 species into 70 families and 191 genera occur in different biogeographical regions of India (Chandra et al. 2008) with the main centres being the Himalayas, the Western Ghats and the Eastern Ghats (Chandra 2000; Dixit 2000). Unfortunately, ferns are

considered as a neglected group of plants in biodiversity as far as their economic value is concerned. However, with the introduction of ethnobotany by Hershberger (1896) for the study of relationship which exists between peoples of primitive societies and their plant environment, numerous attempts were made to study the relationships of pteridophytes with human beings for their medicinal value. Theophrastus (327–287 BC) and Dioscorides (50 AD) cited the medicinal values of pteridophytes. They have been successfully used in the homoeopathic, ayurvedic, unani and tribal systems of medicines (Das 2003; Rout et al. 2009). Ferns had an important role in folklore medicine. Singh (1999) described 160 useful ferns in India based on the pharmacological, phytochemical and ethnobotanical studies. Apart from the medicinal properties, ferns have great aesthetic value for their graceful, delicate beauty and are very good for interior decoration and green houses (Chandra and Kaur 1974).

19.2 Phytochemistry

Plants synthesize a wide variety of chemical compounds which can be sorted by their chemical class, biosynthetic origin and functional groups. The medicinal value of plants lies in chemical substances or group of compounds that produce a definite physiological action in the human body (Edeoga et al. 2005). The beneficial effects of plants are usually due to the secondary metabolites present in it. Medicinal plants contain active ingredients that can be used for therapeutic purposes and are precursors of chemotherapeutical semisynthesis (WHO 1979). It also provides temporary relief to symptomatic problems and health- promoting characteristics and has curative properties. Medicinal plants are under chemical scrutinization due to the advent of modern scientific methods. This leads to the isolation of active compounds. After their isolation and characterization, these active principles in pure form or well-characterized extracts became useful in several countries. Pteridophytes play an important role in the ecological niches of forest ecosystem as an integral part of biogeochemical cycling of minerals. They also help as ecological indicators for the understanding of a particular habitat. Pteridophytes synthesize a wide array of primary and secondary metabolites enriched with various bioactivities to defend and acclimatize various ecological conditions that could potentially be used as an alternative medicine for the treatment of many diseases. However, the available literature on the phytochemicals and their pharmacological applications in pteridophytes are limited. The periodical update on the occurrence, chemotaxonomy and physiological activity of fern secondary metabolites was published by Soeder (1985) and Santos et al. (2010). Irudayaraj and Johnson (2012) summarized the phytochemical and pharmacological studies on spike mosses. Cao et al. (2017) summarized the bioactive phytochemicals and pharmacology of fern species. Baskaran et al. (2018) listed the medicinal uses of ferns. The phytochemical composition and their pharmacological activity of *Athyrium* were summarized by Salehi et al. (2019). In the present review, an attempt is made to provide an update on the phytochemistry of Indian pteridophytes, covering the recent findings concerning the

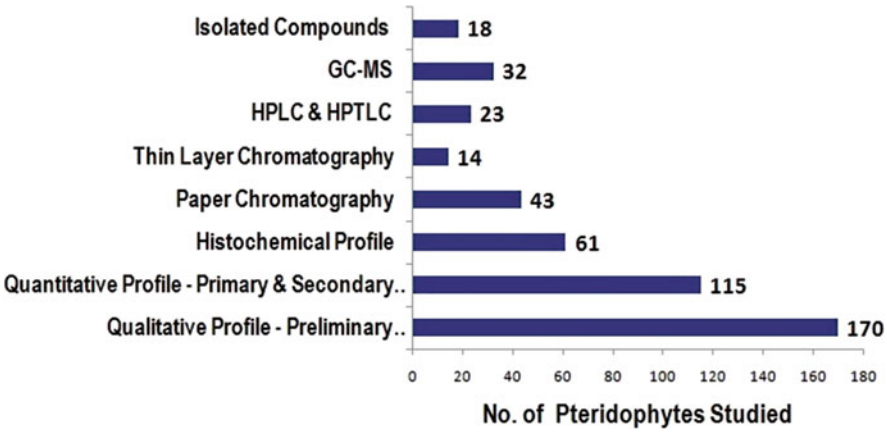

Fig. 19.1 Phytochemistry of Indian pteridophytes

phytochemical composition of crude extracts and their histochemical, spectroscopic and chromatographic profile. Qualitative and quantitative profiles with their primary and secondary metabolites are also included (Fig. 19.1).

19.3 Phytochemistry of Pteridophytes

Plant synthesizes a wide variety of chemical compounds, which can be sorted by their chemical class, biosynthetic origin and functional groups. Many of the phytocompounds provide protection against insect attacks and plant diseases. They also exhibit a number of protective functions for humans. Plants normally produce these secondary metabolites not only to adapt to their environment but also to defend themselves against biotic or abiotic stress, such as high light intensity, extremely high or low temperature, high salinity, drought and natural enemies (Bennett and Wallsgrove 2006). These metabolites are polyphenols, flavonoids, terpenoids, steroids, quinones, alkaloids, polysaccharides and so on (Swain 1977). Ferns are reported to have many useful phytochemicals (secondary metabolites) such as flavonoids, steroids, alkaloids, phenols, triterpenoid compounds, varieties of amino acids and fatty acids (Zeng-fu et al. 2008). In recent years, phytochemical investigations on pteridophytes, especially the ferns, have been progressing steadily and assumed extraordinary importance. The progress in this field led to the development of sophisticated techniques in chemical analysis which can detect even traces of chemical compounds or their precursors in spite being unstable. Quantitative and qualitative estimations of these compounds can be used for finding out which particular fern taxon can be exploited effectively. With increasing awareness or locating additional raw materials for the plant -based industry with particular reference to the sources of proteins, oils, starch, tannins, etc., the knowledge of the distribution pattern of chemical ingredients can play an effective role in exploiting

the plant resources. Knowledge on these phytoconstituents present in plants are used for the discovery of therapeutic agents. Phytochemical studies on pteridophytes attracted the attention of plant scientists due to the ethnomedicinal values. Ferns are expected to have many useful secondary metabolites than other plants.

19.4 Histochemistry of Indian Pteridophytes

Histology is the microscopic study of the structure of biological cells and tissues. Histochemistry is devoted to study the identification and distribution of chemical compounds within and between biological cells, using stains, indicators and light and electron microscopy (Wick 2012). Histochemical methods are employed for qualitative and quantitative analysis of all cellular components including proteins, carbohydrates, lipids, nucleic acids, lignins, tannin, phenolics substances, flavonoids, triterpenoids, etc. (Gahan 1984; Kiernan 1989). Irudayaraj et al. (2014) confirmed the presence of lipids, polyphenols, lignin and tannins in *Lycopodiella cernua*, *Selaginella involvens*, *S. inaequalifolia*, *S. tenera*, *Angiopteris evecta*, *Marattia fraxinea*, *Lygodium microphyllum*, *Pteris argyraea*, *P. confusa*, *Dryopteris concolor*, *Cheilanthes viridis*, *Pellaea boivini*, *Hemionitis arifolia*, *Pityrogramma calomelanos*, *Adiantum raddianum*, *Pteridium aquilinum*, *Histiopteris incisa*, *Hypolepis glandulifera*, *Microlepia speluncae*, *Odontosoria chinensis*, *Lindsaea ensifolia*, *Araiostegia hymenophylloides*, *Nephrolepis multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* and *Cyathea nilgirensis*. Johnson et al. (2014a, b) revealed the histochemical profile, viz. lipids, polyphenols, lignins and tannins, on *Pseudophegopteris pyrrhorhachis*, *Macrothelypteris torresiana*, *Trigonospora ciliate*, *Cyclosorus interruptus*, *Amphineuron terminans*, *Sphaerostephanos arbuscula*, *Christella parasitica*, *C. dentata*, *Asplenium cheilosorum*, *Diplazium muricatum*, *D. travancoricum*, *D. brachylobum*, *Tectaria paradoxa*, *Arachniodes tripinnata*, *A. ambailis*, *A. aristata*, *Dryopteris sparsa*, *Bolbitis appendiculata*, *Blechnum orientale*, *Leptochilus decurrens* and *Pyrrosia porosa*.

Sivaraman and Johnson (2014) localized the polyphenols, lignin and tannins on *S. involvens* (Sto.) Spring, *S. intermedia* (Bl.) Spring, *S. inaequalifolia* (Hook. and Grev.) Spring and *S. tenera* (Hook. and Grev.). SaiLakshmi et al. (2015) revealed the phytochemical constituents of selected *Asplenium* species using histochemical analysis. SaiLakshmi et al. (2015) revealed the existence of lignin, tannin, cutin, suberin and polyphenols in the stipes of *Asplenium aethiopicum*, *A. affine*, *A. decrescens* and *A. viviparum* using histochemical analysis. Vidyarani et al. (2015) revealed the histochemical profiles, viz. lignin, cutin, suberin and polyphenols, on *Adiantum hispidulum*, *A. raddianum*, *A. peruvianum*, *A. pubescens*, *A. tripinnatum* and *A. pacotii*. They recorded varied degree of occurrence of lignin, cutin, suberin and polyphenols in all the studied species. They noted the presence of tannin in all the studied species except *A. raddianum*. Histochemical analysis results revealed the variations in the occurrence of various metabolites, viz. phenolics, tannins and lipids, with varied quantities in different tissues of the rachis. High concentration of lignin,

cutin and suberin presence was observed in the epidermis, hypodermis and xylem of studied pteridophytes. Lignin provides structural rigidity to the plant body and plays a vital defensive role against pathogens and insects.

19.5 Indian Fern Phytochemistry: Preliminary Phytochemical Analysis

As far as Indian pteridophytes are concerned, phytochemical studies have been started by Mehra and Mittal (1960–1961). They screened the Indian species of *Dryopteris* and *Polystichum* for 'filicin' which is used as vermifuge and reported that *Polystichum* lacked 'filicin' completely while *Dryopteris* species gave positive results. Phytochemical analysis on rare, endangered and medicinally important spleenworts, *Asplenium* and *Psilotum*, was investigated by Lal (1979) and Rohtagi et al. (1984). Phytochemical analysis of the edible ferns, *Ampelopteris prolifera* and *Diplazium esculentum*, shows its nutritional value (Shankar and Khare 1985; Singh et al. 1989). Kaur et al. (1986) made a comparative investigation of amino acids and free proline of some Rajasthan ferns.

During the period of 1991–2000, a total of 25 papers were published on the qualitative phytochemical profile. The phytochemical profiles of 61 Indian pteridophytic species, viz. 19 *Thelypteris* sp. of Western Ghats, 3 *Pteris* sp., 3 *Cyathea* sp., 2 *Diplazium* sp., 2 *Adiantum* sp., 3 *Polystichum* sp., 3 *Sphaerostephanos* sp., 3 *Ophioglossum* sp., *Christella* sp., *Tinospora* sp., *Marsilea minuta*, *Diplazium brahylobhum*, *D. polypodioides*, *Pteris vittata*, *Actiniopteris radiata*, *Asplenium pumilum*, *Tectaria macrodonta*, *Cheilanthes farinosa*, *Hypodesmatium crenatum* and *Cyclosorus dentatus*, *Histiopteris incisa*, *Hypolepis glandulifera*, *Microlepia speluncae* and *Pteridium aquilinum*, *Polystichum harpophyllum*, *P. piceopaleaceum* and *P. kunthianum*, were revealed (Chark and Dhir 1991; De Britto et al. 1991; Ramachandran et al. 1991; Rathore and Sharma 1991; Antonisamy et al. 1992; De Britto et al. 1992; Patric Raja et al. 1992; Sharma and Sharma 1992; De Britto et al. 1993; Gopalakrishnan et al. 1993; Jesudass et al. 1993; Henry Joseph et al. 1993; De Britto et al. 1994, a, b, c; Harsh and Sharma 1994; Kumar 1995; Vyas et al. 1995; Yadav 1995 and Irudayaraj 1996). The authors revealed the qualitative and quantitative profile of pigment composition, sugars, starch, amino acids and secondary metabolites of Indian pteridophytes. During this period a good number of ferns have been subjected to preliminary phytochemical screening (Irudayaraj and Raja 1998).

Paulraj (2007) studied the chemical composition of epidermal glands of *S. unitus*, *S. arbuscula* and *S. subtruncatus*. Korwar et al. (2010) revealed the phytochemical profile of *Drynaria quercifolia* Linn rhizome. Talukdar et al. (2010) disclosed the qualitative profile of *Cyathea brunoniana* and *Cyathea gigantea*. *Selaginella* is a rich source of steroids, biflavonoids, alkaloids, secolignans, neolignans and caffeoyl derivatives. Other compounds such as alkaloidal glycosides, phenylpropanones and lignans were also reported (Sa et al. 2012). Phytoprofile of *Blechnum orientale*, *Ceratopteris thalictroides*, *Drymoglossum heterophyllum*, *Dicranopteris linearis*,

Drynaria quercifolia, *Hemionitis arifolia*, *Pityrogramma calomelanos*, *Lindsaea ensifolia*, *Nephrolepis multiflora* and *Pteris confusa* (Mithraja et al. 2012), *Adiantum caudatum*, *A. latifolium*, *A. lunulatum*, *Christella dentata* and *C. parasitica* (Mithraja et al. 2012a), *Acrostichum aureum* (Thomas 2012), *A. capillus-veneris* (Ahmed et al. 2012; Kumar and Nagarajan 2012), *Azolla microphylla* (Abraham and Aeri 2012), *Cyathea gigantea* (Kiran et al. 2012), *H. arifolia* (Bindu et al. 2012) and *Sphenomeris chinensis* (Aceret 2012) are revealed. The authors observed the varied degree of chemical diversity in the studied extracts. The existence of the metabolites is based on the solvents and self-defence mechanism of the ferns. Shakoor et al. (2013) divulged the qualitative phytoprofile of pteridophytes from Shopian district (Jammu and Kashmir), viz. *Adiantum venustum*, *Asplenium adiantum-nigrum*, *A. trichomanes*, *A. pseudofontanum*, *A. septentrionale*, *Athyrium atkinsonii*, *A. attenuatum*, *A. mackinnonii*, *A. wallichianum*, *Azolla cristata*, *Coniogramme affinis*, *Cystopteris fragilis*, *Deparia acuta*, *D. allantodioides*, *Diplazium maximum*, *D. sibiricum*, *Dryopteris blanfordii*, *D. barbigera*, *D. nigropaleacea*, *D. ramosa*, *D. xanthomelas*, *Equisetum arvense*, *Gymnocarpium dryopteris*, *Onychium cryptogrammoides*, *Osmunda claytoniana*, *Phegopteris connectilis*, *Polystichum bakerianum*, *P. discretum*, *P. prescottianum*, *P. yunnanense*, *Pseudophegopteris levingei*, *Pteridium aquilinum*, *Pteris cretica* and *Salvinia natans* aqueous, methanolic, ethanolic and acetone extracts. Phytochemical analysis confirmed the presence of carbohydrates, proteins and free amino acids in 34 species, flavonoids in 27 species, phenolic compounds and tannins in 26 species, glycosides in 24 species, terpenoids in 23 species, saponins in 22 species, volatile oils in 18 species, alkaloids in 15 species, phlobatannins in 12 species and resins in 3 species. Awadhesh Kumar et al. (2014) exposed the phytoprofile for *Adiantum* and *Pteris*. Mismawati et al. (2015) reported the phytochemical constituents of *Angiopteris evecta* leaves methanolic extracts. Ahmed et al. (2015) reported the phytochemical profile of *Drynaria quercifolia*. Kunnathupara et al. (2016) determined the quantitative phytochemical profile of *Azolla microphylla* ethanolic extract.

A good number of preliminary phytochemical analyses were carried out on Indian ferns and fern allies. The available literature on the phytochemical analysis of Indian pteridophytes explains that the phytochemical composition of 170 species belongs to 56 genera and 27 families (Fig. 19.2). The phytochemical analysis on primary and secondary metabolites confirmed the presence of carbohydrates, sugars, reducing sugars, amino acids, proteins, lipids, steroids, saponins, terpenoids, triterpenoids, alkaloids, phenolic compounds, tannins, flavonoids, catechins, glycosides, cardiac glycosides and anthraquinone with varied degree.

19.5.1 Carbohydrates

The presence of carbohydrates is reported in *Isoetes* (Rathore and Sharma 1990), *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum*, *Pteris*

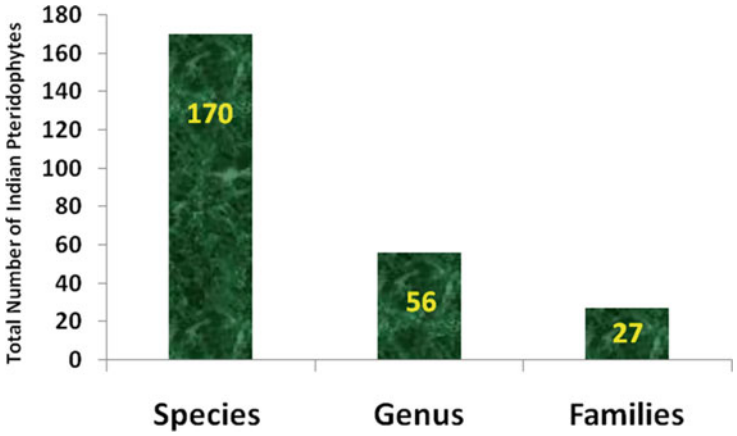

Fig. 19.2 Preliminary phytochemical analysis at family, genus and species level (1960–2021)

vittata, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum*, *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate*, *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Antonisamy 1997; Joseph 1997; Jesudass 1997; Patric Raja 1997), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Tectaria zeylanica* (Sukumaran et al. 2012), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Pteris vittata* (Maneesha et al. 2015), *Dryopteris cochleata* (Das et al. 2015), *Cyathea nilgirensis* (Sahaya Mary and Mahesh 2015), *Salvinia molesta* (Gaya et al. 2016), *Diplazium esculentum* (Dash et al. 2017), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Azolla pinnata* (Thiripurasundari and Padmini 2018), *Azolla pinnata* (Farook et al. 2019), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.2 Sugar

The presence of sugar and reducing sugar in the *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and

D. brachylobum (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Elaphoglossum beddomei* (Maridass and Raju 2010), *Selaginella inaequalifolia* (Irudayaraj et al. (2010), *S. involvens* (Irene Pearl et al. (2011), *S. tenera* (Suganya et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*, *P. confusa*, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Pneumatopteris callosa* (Daryono and Rhomawati 2020) and *Ceratopteris thalictroides* (Smitha and Vadivel 2019) is reported.

19.5.3 Amino Acids

Goswami and Khandelwal (1976) and Khandelwal and Goswami (1976) studied the occurrence of amino acids in different species of Indian *Ophioglossum* while Khare and Shankar (1987) studied the amino acids and proteins in *Psilotum nudum* collected from Pachmarhi. The amino acid profiles of Indian pteridophytes are reported by various localities and researchers, viz. Rajasthan ferns (Kaur et al. 1986). Amino acids existence in the *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*,

Cyathea crinita, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Selaginella* sp. (Paramanik et al. 2002), *Bolbitis appendiculata*, *B. virens*, *Osmunda regalis*, *Ceratopteris thalictroides* and *Drynaria quercifolia* (Kale and Dongarae 2007), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Selaginella involvens* (Irene Pearl et al. 2011), *Diplazium muricatum*, *Diplazium travancoricum* and *Diplazium brachylobum* (Sivaraman et al. 2011), *Pteris argyraea*, *Pteris confusa*, *Pteris vittata*, *Pteris biaurita* and *Pteris multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiate* (Manonmani and Sara 2013), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Pteris vittata* (Maneesha et al. 2015), *Cheilanthes farinosa*, *Cheilanthes anceps*, *Cheilanthes tenuifolia* and *Cheilanthes albomarginata* (Pradnya et al. 2015), *Diplazium esculentum* (Dash et al. 2017) and *Tectaria wightii* (Vineesh et al. 2021) is validated.

19.5.4 Proteins

Proteins are found in *Psilotum nudum* (Khare and Shankar 1987), *Isoetes* (Rathore and Sharma 1990), *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Bolbitis appendiculata*, *B. virens*, *Osmunda regalis*, *Ceratopteris thalictroides* and *Drynaria quercifolia* (Kale and Dongarae 2007), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Tectaria zeylanica* (Sukumaran et al. 2012), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Diplazium esculentum* (Dash et al. 2017), *Adiantum lunulatum* (Jenat and Suresh 2018), *A. aureum* (Arockia Badhsheeba and Vadivel 2020) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.5 Lipids

The available literature confirmed the occurrence of lipids in *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011). Vineesh et al. (2021) confirmed the existence of oils and fats in *Tectaria wightii*.

19.5.6 Steroid

The occurrence of steroids is noted in *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *Dicranopteris linearis* var. *tenuis*, *Dicranopteris linearis* var. *brevis*, *Blechnum orientale*, *Blechnum occidentale*, *Nephrolepis multiflora*, *Cyathea crinita*, *Cyathea nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *S. inaequalifolia* (Irudayaraj et al. 2010), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Selaginella involvens* (Irene Pearl et al. 2011), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *Selaginella tenera* (Suganya et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*,

P. confusa, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Tectaria zeylanica* (Sukumaran et al. 2012), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Bolbitis virens*, *B. appendiculata* and *B. presliana* (Manisha 2015), *Salvinia molesta* (Nithya et al. 2015), *Dryopteris cochleata* (Das et al. 2015), *Drynaria quercifolia* (Padhy and Dash 2015), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Adiantum capillus-veneris* (Ranjan and Vats 2016), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Azolla pinnata* (Thiripurasundari and Padmini 2018), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Asplenium aureum* (Arockia Badhsheeba and Vadivel 2020) and *Sphaerostephanos unitus* (Johnson et al. 2020a, b, c).

19.5.7 Saponins

The available literature confirmed the presence of saponins in *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Nephrolepis multiflora*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *Elaphoglossum beddomei* (Maridass and Raju 2010), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Selaginella involvens* (Irene Pearl et al. 2011), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *Christella parasitica* (Paulraj et al. 2011), *Tectaria zeylanica* (Sukumaran et al. 2012), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Nephrolepis cordifolia* (Rukmini and Suvarnalatha 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Lygodium flexuosum*

(Singh 2017), *Salvinia molesta* (Nithya et al. 2015), *Drynaria quercifolia* (Padhy and Dash 2015), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Salvinia molesta* (Gaya et al. 2016), *Adiantum capillus-veneris* (Ranjan and Vats 2016), *Stenochlaena palustris* (Arullappan et al. 2017), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Adiantum lunulatum* (Jenat and Suresh 2018), *Azolla pinnata* (Thiripurasundari and Padmini 2018; Farook et al. 2019), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *A. aureum* (Arockia Badhsheeba and Vadivel 2020), *Adiantum philippense* (Adnan et al. 2020), *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.8 Terpenoids and Triterpenoids

Tectaria paradoxa, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Leptochilus decurrens* f. *lanceolatus* and *L. decurrens* (Patricraja 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *S. inaequalifolia* (Irudayaraj et al. 2010), *Elaphoglossum beddomei* (Maridass and Raju 2010), *S. involvens* (Irene Pearl et al. 2011), *Asplenium affine*, *A. decrescens* and *A. zenkeranum* (Irudayaraj and Johnson 2011), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *S. tenera* (Suganya et al. 2011), *Christella parasitica* (Paulraj et al. 2011), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Pyrrosia lanceolata* (Ruby and Sara 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Dryopteris cochleata* (Das et al. 2015), *Pteris vittata* (Maneesha et al. 2015), *Salvinia auriculata* (Suvarnalatha et al. 2015), *S. molesta* (Nithya et al. 2015), *Adiantum capillus-veneris* (Ranjan and Vats 2016), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Salvinia molesta* (Gaya et al. 2016), *A. latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Diplazium esculentum* (Dash et al. 2017), *Stenochlaena palustris* (Arullappan et al. 2017), *Adiantum lunulatum* (Jenat and Suresh 2018), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Azolla pinnata* (Farook et al. 2019), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Pneumatopteris callosa* (Daryono and Rhomawati 2020), *A. aureum* (Arockia Badhsheeba and Vadivel 2020) and *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c) showed the existence of terpenoids and triterpenoids in the ferns and fern allies of India.

19.5.9 Alkaloids

The existing literature authenticated the existence of alkaloids in the crude extracts of *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *Elaphoglossum beddomei* (Maridass and Raju 2010), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Asplenium affine*, *A. decrescens* and *A. zenkeranum* (Irudayaraj and Johnson 2011), *Christella parasitica* (Paulraj et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*, *P. confusa*, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. (2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Nephrolepis cordifolia* (Rukmini and Suvarnalatha 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Pteris vittata* (Maneesha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Bolbitis virens*, *B. appendiculata* and *B. presliana* (Manisha 2015) *Cyathea gigantea* (Manisha 2015), *Selaginella bryopteris* (Jyothi et al. 2015), *Dryopteris cochleata* (Das et al. 2015), *Actiniopteris radiata* (Mathad and Modi 2015), *Salvinia molesta* (Nithya et al. 2015), *Lygodium flexuosum* (Singh 2017), *Cyathea nilgirensis* (Mary and Mahesh 2015), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Salvinia molesta* (Gaya et al. 2016), *Stenochlaena palustris* (Arullappan et al. 2017), *Pneumatopteris callosa* (Daryono and Rhomawati 2020), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Azolla pinnata* (Farook et al. 2019), *Adiantum philippense* (Adnan et al. 2020) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.10 Phenolics Compounds

The phenolics are found in *Selaginella* (Bohra et al. 1979), *Isoetes* (Rathore and Sharma 1990), *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and

D. brachylobum (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Nephrolepis multiflora*, *Cyathea crinita*, *Cyathea nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *S. lepidophylla* (Chikmawati and Miftahudin 2008), *S. inaequalifolia* (Irudayaraj et al. 2010), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *S. tenera* (Suganya et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*, *P. confusa*, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Pyrrosia lanceolata* (Ruby and Sara 2014), *Nephrolepis cordifolia* (Rukmini and Suvarnalatha 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Pteris vittata* (Maneesha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Bolbitis virens*, *B. appendiculata* and *B. presliana* (Manisha 2015), *Selaginella bryopteris* (Jyothi et al. 2015), *Dryopteris cochleata* (Das et al. 2015), *Actiniopteris radiata* (Mathad and Modi 2015), *Salvinia molesta* (Nithya et al. 2015), *Drynaria quercifolia* (Padhy and Dash 2015), *Adiantum capillus-veneris* (Ranjan and Vats 2016), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Salvinia molesta* (Gaya et al. 2016), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Stenochlaena palustris* (Arullappan et al. 2017), *Adiantum lunulatum* (Jenat and Suresh 2018), *Azolla pinnata* (Thiripurasundari and Padmini 2018), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Azolla pinnata* (Farook et al. 2019), *Acrostichum aureum* (Arockia Badhsheeba and Vadivel 2020), *Adiantum philippense* (Adnan et al. 2020) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.11 Tannins

The tannins showed their presence in the crude extracts of *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Nephrolepis multiflora*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *S. inaequalifolia* (Irudayaraj et al. 2010), *Elaphoglossum beddomei* (Maridass and Raju 2010), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *Christella parasitica* (Paulraj et al. 2011), *Selaginella tenera* (Suganya et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*, *P. confusa*, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Tectaria zeylanica* (Sukumaran et al. 2012), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Nephrolepis cordifolia* (Rukmini and Suvarnalatha 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Pteris vittata* (Maneesha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Bolbitis virens*, *B. appendiculata* and *B. presliana* (Manisha 2015), *Selaginella* bryopteris (Jyothi et al. 2015), *Actiniopteris radiata* (Mathad and Modi 2015), *Salvinia molesta* (Nithya et al. 2015), *Drynaria quercifolia* (Padhy and Dash 2015), *Adiantum capillus-veneris* (Ranjan and Vats 2016), *Diplazium esculentum* (Dash et al. 2017), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Stenochlaena palustris* (Arullappan et al. 2017), *Adiantum lunulatum* (Jenat and Suresh 2018), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Pneumatopteris callosa* (Daryono and Rhomawati 2020), *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.12 Flavonoids

Flavonoids existence was observed in the crude extracts of *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *C. crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus* (Patric Raja 1997), *Selaginella lepidophylla* (Chikmawati and Miftahudin 2008), *Azolla pinnata*, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *Asplenium affine*, *A. decrescens* and *A. zenkeranum* (Irudayaraj and Johnson 2011), *Christella parasitica* (Paulraj et al. 2011), *Adiantum lunulatum*, *A. capillus-veneris*, *Pteris otaria*, *P. aspericaulis*, *P. kleiniana*, *P. confusa*, *P. multiaurita*, *P. vittata*, *Asplenium polyodon* and *Hypodematium crenatum* (De Britto et al. 2012a), *Pteris argyraea*, *P. confusa*, *P. vittata*, *P. biaurita* and *P. multiaurita* (Herinsheeba et al. 2013), *Actiniopteris radiata* (Manonmani and Sara 2013), *A. radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Nephrolepis cordifolia* (Rukmini and Suvarnalatha 2014), *Salvinia auriculata* (Suvarnalatha et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Pradnya et al. 2015), *Selaginella bryopteris* (Jyothi et al. 2015), *Actiniopteris radiata* (Mathad and Modi 2015), *Dryopteris cochleata* (Das et al. 2015), *Salvinia molesta* (Nithya et al. 2015), *Drynaria quercifolia* (Padhy and Dash 2015), *Cyathea nilgirensis* (Sahaya Mary and Mahesh 2015), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Salvinia molesta* (Gaya et al. 2016), *Adiantum capillus-veneris* (Ranjan and Vats (2016), *Diplazium esculentum* (Dash et al. 2017), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017), *Stenochlaena palustris* (Arullappan et al. 2017), *Azolla pinnata* (Thiripurasundari and Padmini 2018), *Pneumatopteris callosa* (Daryono and Rhomawati 2020), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Acrostichum aureum* (Arockia Badhsheeba and Vadivel

2020), *Adiantum philippense* (Adnan et al. 2020), *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c) and *Tectaria wightii* (Vineesh et al. 2021).

19.5.13 Catechins

The presence of catechins was documented in the crude extracts of *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* (Antonisamy 1997), *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum* (Jesudass 1997), *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximate* (Joseph 1997), *Selaginella inaequalifolia* (Irudayaraj et al. 2010), *Selaginella involvens* (Irene Pearl et al. 2011), *Actiniopteris radiata* (Manonmani and Sara 2013) and *Pyrrosia lanceolata* (Ruby and Sara 2014).

19.5.14 Glycosides and Cardiac Glycosides

The available literature confirms the occurrence of glycosides in the crude extracts of *Diplazium muricatum*, *D. travancoricum* and *D. brachylobum* (Sivaraman et al. 2011), *Pyrrosia lanceolata* (Ruby and Sara 2014), *Selaginella bryopteris* (Rupa and Bhavani 2014), *Bolbitis virens*, *B. appendiculata* and *B. presliana* (Manisha 2015), *Cyathea gigantea* (Manisha 2015), *Dryopteris cochleata* (Das et al. 2015), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Stenochlaena palustris* (Arullappan et al. 2017), *Adiantum lunulatum* (Jenat and Suresh 2018), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019), *Ceratopteris thalictroides* (Smitha and Vadivel 2019), *Acrostichum aureum* (Arockia Badhsheeba and Vadivel 2020) and *Adiantum philippense* (Adnan et al. 2020). The cardiac glycosides existence is confirmed in *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015a, b), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Adiantum latifolium*, *Angiopteris evecta* and *Marattia fraxinea* (Chandra et al. 2017) and *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c).

19.5.15 Anthraquinone

The anthraquinone presence was reported in *Lastreopsis tenera*, *Polystichum piceopaleaceum*, *Arachniodes tripinnata*, *Dryopteris madrasensis*, *D. approximata*, *D. cochleata*, *D. sparsa* (Joseph 1997) and *Ceratopteris thalictroides* (Smitha and Vadivel 2019).

19.5.16 Coumarin

Azolla pinnata, *Marsilea minuta* and *Salvinia molesta* (Mithraja et al. 2011), *Tectaria zeylanica* (Sukumaran et al. 2012), *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Ceratopteris thalictroides* (Smitha and Vadivel 2019) and *Azolla pinnata* (Farook et al. 2019) crude extracts showed the presence of coumarin.

19.5.17 Betacyanin

The presence of betacyanin is reported in *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b) and *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b).

19.5.18 Quinone

The existing literature confirms the occurrence of quinine in *Azolla pinnata*, *Marsilea minuta and Salvinia molesta* (Mithraja et al. 2011), *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpana Devi et al. 2014a, b), *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b), *Salvinia molesta* (Nithya et al. 2015), *Asplenium indicum*, *Lepisorus nudus* and *Microsorum membranaceum* (Jadhav et al. 2019) and *Ceratopteris thalictroides* (Smitha and Vadivel 2019) crude extracts.

Phytochemical analysis has been done on a large number of Indian fern and fern allies. But the majority of the reports pertain to quantitative estimation of primary metabolites which are universal in occurrence and are highly variable with the environment. Figure 19.3 summarized the preliminary phytochemical studies on Indian pteridophytes.

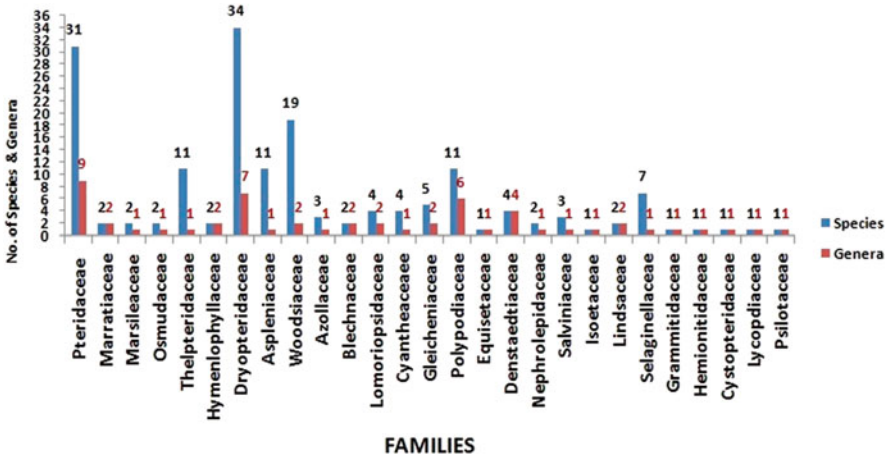

Fig. 19.3 Phytochemical studies on Indian pteridophytes: f amily, genus and species level

19.6 Chromatographic Studies on Pteridophytes

Plant extracts are evaluated by different biological methods to find out the pharmacological activity. Qualitative and quantitative chemical examination is designed to detect and isolate the active ingredients (AOAC 2005). Due to the advances in analytical instrumentation, the quantitative determination of phytochemicals is made very easy. Recent developments in the isolation, purification and structure elucidation of naturally occurring metabolites have made it possible to establish appropriate strategies for the process of standardization. The modern pharmacognosist adapt various analytical tools for the quality assessment of the crude drugs, which includes fluorescence, spectroscopic (UV-Vis, FT-IR, MS, NMR), chromatographic (paper, TLC, HPLC, HPTLC and GC-MS) and electrophoretic analysis. The results from these sophisticated techniques provide a chemical fingerprint as to the nature of chemicals or impurities present in the plant extract (Bilia et al. 2002; Rozylo et al. 2002; WHO 2002). The chromatographic techniques are accepted as a strategy for identification and evaluation of the quality of plant medicines (Farnsworth et al. 1985). In chemotaxonomy, they are used to distinguish the medicinal sources from its adulterants and standardization of plant products and are used as taxonomic tool to classify the medicinal plants. Information on these chemical constituents not only aid in discovering new therapeutic drugs, but such information can also help in disclosing new sources of economic materials which are precursors for the synthesis of complex chemical substances (Farnsworth 1996). In the recent years, advancement in chromatographic and spectral fingerprints plays an important role in the quality control of complex herbal medicines. Chemical fingerprints obtained using chromatographic methods are used not only for the purpose of quality control of herbal medicines but also for authentication and identification of herbal plant.

Amino acids and sugar profiles of *Tectaria paradoxa*, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximata*, *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis, P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa*, *Acrostichum aureum*, *Dryoathyrium boryanum*, *Athyrium puncticaule*, *Athyrium solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum* have been studied by ascending and descending types of paper chromatographic methods (Antonisamy 1997; Joseph 1997; Jesudass 1997). They calculated the paired affinity indices of sugar and amino acids among the studied ferns by the method described by Ellison et al. (1962). These profiles are employed as marker to differentiate the species, and these profiles solved the taxonomical conflict between and among the ferns.

TLC and HPTLC are efficient tools for the phytochemical evaluation and widely accepted technique for its high accuracy, precision and reproducibility of results. It has many advantages because of high sample throughput at low operating cost, easy sample preparation, short analysis time and analytical assurance (Liebler et al. 1996). TLC has the special ability to assay many samples at the same time on a single plate. TLC enables trustworthy separation and analysis of compounds from a wide range of classes in many types of biological samples (Sherma and Fried 2005). TLC enables reliable separation and analysis of compounds from a wide variety of classes in many types of biological samples (Sherma and Fried 2005). Fingerprint analysis approach using HPTLC has become the most potent tool for quality control of herbal medicines because of its simplicity and reliability (Bobby et al. 2012). It can serve as a tool for identification, authentication and quality control of herbal drugs (Prema et al. 2015). HPTLC is utilized for linking the chemical constituents of the plant with high proficiency which in turn provides unique profiling of that particular plant (Bobby et al. 2012). It is more efficient and faster, and the results are more reliable and reproducible. HPTLC provides the record of separation in the form of a chromatogram with fractions represented as peaks with defined parameters including absorbance (intensity), R_f, height and area. Furthermore, the feature of a pictorial fluorescence image of HPTLC coupled with a digital scanning profile is more attractive to herbal analysts for constructing a herbal chromatographic fingerprint. These provide adequate information and parameters for comprehensive identification, assessment and comparison of major active constituent fingerprints in the samples, and it serves as a basis for their use in medicinal preparations. By using chromatographic fingerprints, the authentication of herbal medicines can be accurately conducted even if the amount or concentration of the chemical constituents is not exactly the same for different samples of drug.

Saito et al. (1989) reported the distribution of ptaquiloside and ptaquiloside-like compounds in Pteridaceae by chemical assay (TLC) and observed the widespread occurrence in a variety of ferns, viz. *Cheilanthes myriophylla*, *Cibotium barometz*, *Dennstaedtia scabra*, *Histiopteris incisa*, *Pityrogramma calomelanos*, *Pteris*

cretica, *P. nipponica*, *P. oshimensis*, *P. tremula* and *P. wallichiana*. Sharma and Sharma (1992) identified various flavonoids in eight different ferns from Rajasthan by paper chromatography. Krishna and Dawra (1994) reported ptaquiloside in *Pteris quadriaurita* and *Onychium contiguum* for the first time in India by TLC method. Dalli et al. (2007) studied the methanolic extract of *Pteris biaurita* using TLC bioassay, and the active fraction exposed the inhibition zone with R_f value 0.5–0.65. Irudayaraj and Johnson (2011) revealed the interspecific relationship among *Asplenium affine*, *A. decrescens* and *A. zenkeranum*. Pathania et al. (2012) analysed the flavonoid quercetin in various ferns growing in northern India using TLC. The existence of quercetin in *Christella arida*, *Deparia japonica*, *Dryopteris cochleata*, *D. juxtaposita*, *Hypodematium crenatum*, *Polystichum squarrosum* and *Pteridium revolutum* is confirmed using TLC. Chikmawati et al. (2012) divulged the alkaloids, flavonoids and steroids profile of *Selaginella* species. Mandal and Mondal (2012) analysed the free amino acids present in the leaf glands of pteridophytes using TLC. DL-methionine is the common free amino acid of *Pteris vittata*, *Drynaria quercifolia*, *Ampelopteris prolifera* and *Dryopteris filix-mas*. L-tyrosine monohydrochloride is common in *D. filix-mas* and *Selaginella indica*. L-arginine monohydrochloride is also common in *D. quercifolia*, *Ceratopteris thalictroides* and *Marsilea quadrifolia*. Glycine is the only amino acid found in *Helminthostachys zeylanica*. Pauline Vincent et al. (2012) determined the phytochemical profile for *A. terminans*, *C. parasitica* and *C. interruptus* using TLC. Johnson et al. (2013) revealed the phenolic and steroid profile of two varieties of *Blechnum orientale* L., viz. var. *grandis* and var. *orientale*. Selvaraj et al. (2013) isolated bioactive polyphenolic compounds from methanolic extract of *Azolla microphylla*. Ranjan and Vats (2016) confirmed the presence of diverse type of phytochemicals in *Adiantum capillus-veneris* using TLC. Singh (2017) revealed the TLC profile of *Lygodium flexuosum* ethanolic extract.

Sharad et al. (2008) and Srivastava et al. (2008) disclosed the phytochemical composition of *Lycopodium clavatum* using HPTLC and observed the presence of ferulic acid. Pauline Vincent et al. (2012) determined the phytochemical profile for *A. terminans*, *C. parasitica* and *C. interruptus* using HPTLC. The phenolics and flavonoids HPTLC profile of *Pteris vittata* was determined (Paul and Banerjee 2013). Selvaraj et al. (2013) isolated and quantified the rutin and quercetin from methanolic extract of *Azolla microphylla*. Shweta et al. (2013) determined the interspecific variation among four *Adiantum* species using HPTLC profile. Sivagurunathan and Xavier Innocent (2014) revealed the presence of 11 compounds from *Marsilea quadrifolia*. HPTLC fingerprinting of rhizome extracts of *Dryopteris cochleata* showed several peaks with different R_f values (Das et al. 2015). Janakiraman and Johnson (2016a, b) revealed the HPTLC phenolics, flavonoids and tannins profile of *Cyathea nilgirensis*, *C. gigantea* and *C. crinita*. Johnson et al. (2020b, b, c) validated and revealed the phenolic, flavonoids, alkaloids and tannins profile of *Asplenium aethiopicum* (Burm. f.) Becherer methanolic extracts using HPTLC. The observed profile will help us to identify the crude drugs and improve the therapeutic potentials of *A. aethiopicum*. In addition, the TLC and HPTLC profiles will be used as phytomarker to distinguish the drug from its adulterants.

These profiles play a vital role in chemosystematic to find a solution for the taxonomical problems.

HPLC is a highly sensitive method for detection, identification and quantification of any chemical in a particular sample using UV and visible absorbance (Hanachi and Golkaho 2009). HPLC offers advantages in identifying the isolated compounds (Zhang et al. 2010) and in the quantitative determination (Douat et al. 2011). HPLC is an important qualitative and quantitative technique generally used for quality control testing and estimation of pharmaceutical and biological samples (Guillaume and Veuthey 2012; Snyder et al. 2009; Ahuja and Rasmussen 2007). De Britto et al. (1994) performed the HPLC studies on the species of Thelypteridaceae and produced the phytomarker for the studied ferns.

HPLC analysis of *Pteris biaurita* following elution from TLC plate revealed a single peak with the retention time of 8.1 min (Dalli et al. 2007). Paulraj et al. (2011) studied the presence of various kinds of terpenoids, alkaloids, tannins, saponins and flavonoids on the epidermal glands extract of the glandular morphotype *Christella parasitica* using HPLC. Mostafa and Ibrahim (2012) analysed α-tocopherol in *Azolla caroliniana* using HPLC which showed great quantitative variations, where as ascorbic acid and β-carotene showed marked changes in both number and area of the characterized peaks subjected to UV-B. Chikmawati et al. (2012) determined the highest amentoflavone (6.87 ppm) content in *Selaginella subalpina* using HPLC analysis. Pathania et al. (2012) quantified the carcinogen and ptaquiloside in various ferns growing in certain enzootic areas of Himachal Pradesh and Uttarakhand. The presence of ptaquiloside in *Dryopteris cochleata*, *Hypodematium crenatum*, *Pseudocyclosorus canus* and *Pteris cretica* was identified and quantified. Pauline Vincent et al. (2012) determined the phytochemical profile for *A. terminans*, *C. parasitica* and *C. interruptus* using HPLC. Selvaraj et al. (2013) isolated bioactive polyphenolic compounds from methanolic extract of *Azolla microphylla* using HPLC. Kamboj and Kalia (2014) studied the detailed pharmacognostical parameters for the histological and physicochemical standardization of *Drynaria quercifolia* using HPTLC and HPLC methods. Jaishee and Chakraborty (2015) identified the phenolics, viz. catechin, caffeic, ferulic, salicylic and vanillic acid occurrence in *P. vittata* and *D. linearis* by HPLC analysis.

Knowledge of the chemical constituents of plants is used for the discovery of therapeutic agents, and this information may be helpful in finding new sources of economically important phytocompounds for the synthesis of complex chemical substances (Milne 1993). Mass spectrometry, coupled with chromatographic separations such as gas chromatography (GC-MS), is normally used for direct analysis of components existing in traditional medicines and medicinal plants. GC-MS is a powerful technique having many applications including high sensitivity and specificity. The combination of a principle separation technique (GC) with the best identification technique (MS) made GC-MS ideal for qualitative and quantitative analysis for volatile and semi-volatile compounds (Karthishwaran et al. 2012). GC-MS is proved to be an effective tool for analysing medicinal plants for the presence of non-polar components, volatile essential oil, fatty acids, lipids, etc. (Jie and Choi 1991) and alkaloids (Bertz et al. 1997). Kurumatani et al. (2001) isolated

the gibberellins A_{73} methyl ester, the most abundant antheridiogen, and the methyl esters of GA_9 and several monohydroxy GA_{73} derivatives from the schizaeaceous ferns *Lygodium microphyllum* and *Lygodium reticulatum*. Ramesh et al. (2001) isolated friedelin, epifriedelinol, β-amyrin, β-sitosterol, β-sitosterol 3-β-D-glucopyranoside and naringin from the dried rhizome of *Drynaria quercifolia*. Juliani et al. (2004) detected the presence of sesquiterpenes (75%) with lower amounts of monoterpenes. Niko et al. (2006) identified 25 compounds in *Equisetum arvense* stem essential oil. Hashemi et al. (2007) studied the volatile components of *Artemisia aucheri* using GC-MS which includes 1,8-cineole, chrysanthenone, α-pinene and mesitylene. Choudhary et al. (2008) isolated two glycosides, viz. 6′-O-(3,4-dihydroxy benzoyl)-β-d-glucopyranosyl ester and 4-O-β-d-glucopyranoside-3-hydroxy methyl benzoate, along with five known compounds, viz. methyl benzoate, hypogallic acid, caffeic acid, paeoniflorin and pikuroside from a fresh water fern *Salvinia molesta* showing potent antioxidant radical scavenging activity.

Kumar et al. (2011) reported more than 13 individual compounds from *Polypodium decumanum* ethanolic extracts, and the main compound identified was long -chain fatty acids along with the flavonoids. Dubal et al. (2013) identified the presence of octadec-9 -enoic acid (oleic acid), n- hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), di-n-octyl phthalate, hexadecanoic acid methyl ester, hexadecanoic acid and ethyl ester from the methanolic extracts of *Tectaria coadunata* rhizome. Babu (2013) confirmed the metabolites namely Pentadecanoic acid, 14-methyl-, methyl ester, Hexadecanoic acid, methyl ester, 9, 12-Octadecadienoic acid, methyl ester, (E, E)- 4) 9, 12-Octadecadienoic acid, methyl ester, 9-Octadecenoic acid (Z)-, methyl ester, Octadecanoic acid, methyl ester, Squalene and 4, 8,12,16-Octadecatetraen-1-ol,4,9,13,17-tetramethyl presence in *Adiantum latifolium*, 3,7,11,15-Tetramethyl-2-hexadecen-1-ol, 4 Cyclopropylcarbonyloxydodecane, Phytol, 1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester and Squalene existence in *Acrostichum aureum*, 6-Octen-1-ol, 3,7-dimethyl-,propanoate (Synonym-Citronellyl propionate), Phytol and Squalene presence in C. interruptus and 1,8-Octanediol, Naphthalene, 1-butyl-1,2,3,4-tetrahydro-4-pentyl, 1-Indanone, 3,3,4,5,7-Pentamethyl, Phytol and Squalene existence in *Histiopteris incisa* using GC-MS analysis. Kumar et al. (2014) identified 5 -7A-isoprpenyl-4, 5-dimethyloctahydro-1 h-inden-4yl)-3-methyl-2-penta (24.49%), n-hexadecanoic acid (18.29%), gamma-sitosterol (10.61%) and cis-vaccenic acid (9.25%) from the methanolic extracts of *Adiantum capillus-veneris*. Rukmini and Suvarnalatha (2014) observed the existence of neophytadiene and 2,6,10-trimethyl,14,ethylene,2 hexadecen-1-ol and 3,7,11,15 tetramethyl RR, hexadecanoic acid, palmitic acid, 9 -octadecenoic acid (Z)-, oleic acid, octadecanoic acid, stearic acid, stigmast-4-en-3-one and 4-stigmasten-3-one from *Nephrolepis cordifolia*.

Santhosh et al. (2014) identified the presence of 5- 7A-isoprpenyl-4, 5-dimethyloctahydro-1 h-inden-4yl)-3-methyl-2-penta, n-hexadecanoic acid, gamma-sitosterol, cis-vaccenic acid (9.25%), 5-7A-isopropenyl-4,5-dimethyl-octahydro-inden-4-yl)-3-methyl-pent-2-EL, tetradecanoic acid and phenanthrene in the methanolic extracts of *Adiantum capillus-veneris*. Sivagurunathan and Xavier

(2014) reported the existence of hexadecanoic acid, ethyl ester, phytol, 9,12-octadecadienoic acid (Z,Z), 1,2-benzenedicarboxylic acid, diisooctyl ester, 3,7,11,15-tetramethyl-2-hexadecen-1-ol, 2(3H)-furanone, dihydro-3-hydroxy-4,4-dimethyl and octadecanoic acid, ethyl ester in the ethanolic extract of *Marsilea quadrifolia*. Prasanna and Chitra (2014) studied the phytochemical constituents and chemical composition of *Drynaria quercifolia* rhizome methanolic and petroleum ether extracts.

Karikalan and Rajangam (2014) reported the occurrence of 4H-pyran-4-one,2,3-dihydro-3,5-dihydroxy-6-methyl, n-hexadecanoic acid, 9,12,15-octadecatrienoic acid, methyl ester (Z,Z,Z), 2-furancarboxaldehyde, 5-(hydroxymethyl), 4H-pyran-4-one and 2, 3-dihydro-3, 5-di hydroxy-6-methyl from *Marsilea quadrifolia*. Rukmini et al. (2015) validated the presence of mesityl oxide, 2- pentanone, benzene, neophytadiene, phytol, oleic acid, stearic acid and stigmast-4-en-3-one in the acetone extracts of *Hemionitis arifolia*.

GC-MS analysis of *Salvinia molesta* confirmed the presence of bioactive components apiol, hexadecanoic acid, pentadecanoic acid and octadecatriene (Nithya et al. 2015). Manonmani and Catharin Sara (2015) revealed the existence of hexadecanoic acid, ethyl ester (20.40%), 9,12-octadecadienoic acid, methyl ester, (E,E), (E)-9-octadecenoic acid ethyl ester, docosanoic acid, ethyl ester and heptadecanoic acid heptadecyl ester in *A. radiata*. Kanchan et al. (2015) reported the occurrence of germacrene D; 1, 3- cyclohexanedione, 2- methyl −2- (3-o xobutyl); and neoisolongifolene, 8, 9- dehydro 7 from *Tectaria coadunata* ethanolic extract. Pradnya et al. (2015) reported the presence of 3, 7, 11, 15 -tetramethyl-2-hexadecen-1-ol, n- hexadecanoic acid, ethyl ester 9-octadecenoic acid, 1, 2-benzenedi carboxylic acid, discotyl ester, n-tetracontane and diploptene in the *Cheilanthes farinosa* ethanolic extracts. Kunnathupara et al. (2016) determined the presence of 2-butanone, 3-methoxy-3-methyl, 2,2-dimethyl propionic acid, cyclopentyl ester, butane, 1-bromo-2-methyl, 2-hexen-1-ol,2-ethyl, 5-hydroxy-2,2-dimethyl hexan-3-one, phthalic acid, ethyl pentyl ester and pentanoic acid, 2-methyl from *Azolla microphylla*. Janakiraman and Johnson (2016a, b) revealed the presence of methyloctadecyl dichlorosilane and 2-methylbutane-1,4-diol in *C. nilgirensis*, 3-(1-ethoxyethoxy) in *C. gigantea* and 2-hydroxy-5-methylbenzaldehyde in *C. crinita*. GC-MS analysis of *Acrostichum aureum* revealed five phytosterols, viz. campesterol, stigmasterol, γ-sitosterol, cycloartanol, methylene and cycloartanol (Anitta et al. 2016). Quercetin, 7, 3, 4 -trimethyl ether, phytol, feren-8-ene and hexadecanoic acid are reported from the methanolic extract of *Dicranopteris linearis* (Kalpana Devi et al. 2016a, b). Nayak and Padhy (2017) revealed the presence of gliricidin7-O-hexoside, quercetin-7-O-rutinoside, kaempferol-3-O-rutinoside and myricetin-3-O-rhamnoside from *A. caroliniana* and the major compound 3-O-methyl -d-glucose with peak area 91.89% (Jarial et al. 2018b, b). GC-MS analysis of methanolic extract of *Adiantum capillus-veneris* identified major bioactive phytochemical compounds, viz. dodecanoic acid, nonadecane, tetradecanoic acid, 3,7,11,15-tetramethyl-2-hexadecen-1-ol, acetic acid, 3,7,11,15-tetramethyl-hexadecyl ester, docosane, 1,2-benzenedicarboxylic acid, butyl octyl ester, n-hexadecanoic acid, 9-octadecenoic acid, di-n-octyl phthalate and tetracontane

(Chhaya et al. 2020). Vineesh et al. (2021) validated the presence of octadec-9-enoic acid (oleic acid), n-hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), di-n-octyl phthalate, hexadecanoic acid methyl ester and hexadecanoic acid ethyl ester from *Tectaria wightii*.

19.7 Spectroscopic Studies on Indian Pteridophytes

Spectroscopic (UV-Vis and FT-IR) methods together or separately can be used as a predictable method for detection of biomolecular composition (Socaciu et al. 2005; Schultz and Baranska 2007; Ibrahim and Osman 2009). FT-IR is one of the most widely used methods to identify the functional groups and pave a way to elucidate the compounds structures. It has been used as a requisite method to identify medicines in pharmacopoeia of many countries (Liu et al. 2006). FT-IR is a rapid, non-destructive technique with minimum sample preparation necessary (Smith 2011). It allows the qualitative determination of organic compounds as the appearance of the bands in the infrared spectrum. Sant et al. (2013) reported FT-IR analysis of *Adiantum philippense* frond to identify the biogroups that bound distinctively on the gold and silver surface. The major peaks observed in FT-IR of the extract were 3369, 2360, 1585, 1384, 1076 and 514 cm^{-1}. Peak at 3369 cm^{-1} is attributed to OH stretch in phenols. Gowtham (2013) analysed the UV-Vis spectra of different extracts of *Asplenium aethiopicum* and identified the presence of metabolites and the functional groups. The results of FT-IR analyses confirmed the presence of alkanes, esters, primary amines alkyl halides, carboxylic acids and secondary amines in *Asplenium aethiopicum*.

Janakiraman and Johnson (2014) performed UV-Vis spectroscopic analysis for different extracts of *Cyathea nilgirensis*, *C. gigantea* and *C. crinita*. They used macroscopical fingerprint characters not only to identify the chemical constituents but also to distinguish the morphologically similar species of *Cyathea*. Janakiraman and Johnson (2015a, b) revealed the functional groups present in *C. nilgirensis*, *C. gigantea* and *C. crinita* using FT-IR. The analytical evaluation of the FT-IR spectra exposed the significant differences in band position and absorbance intensities. The comparative FT-IR spectra showed that there is an apparent change in relative intensity of the bands. Prasanna and Anuradha (2016) analysed the FT-IR profile of methanolic extracts of *Drynaria quercifolia* rhizome and confirmed the presence of amines, alkanes, denatured amines, alkynes, carboxylic acids and alkenes. John Peter Paul (2018) revealed the FTIR profile of *Blechnum orientale* methanolic extract and confirmed the presence of functional groups such as aldehydes, monosubst benzenes, 1, 2, 4 trisubstituted benzenes, organophosphorus, siloxanes, pyridine- n- oxides, aliphatic nitro, amino acids, hydrochlorides, amino acid esters, aliphatic and aromatic primary amines. In addition, spectroscopic methods are employed to quantify the secondary metabolites of ferns (Johnson et al. 2020b, b, c) and to confirm the plant extracts mediated nanoparticle synthesis (Johnson et al. 2017a, b, 2020b, b, c).

The quantity of chlorophylls, carotenoids and phenolics is estimated in drought resistance ferns and fern allies (*Selaginella*) from Rajasthan (Bohra et al. 1979; Vyas et al. 1989). Yadav (1990) estimated the proline of five *Ophioglossum* species growing in Rajasthan. Rathore and Sharma (1990) determined the soluble proteins, total phenols and carbohydrates on three species of *Isoetes* collected from Rajasthan. Phytochemical composition of Rajasthan ferns and fern allies was determined by Kaur et al. (1986); Vyas and Sharma (1988); Sharma (1989); and Rathore and Sharma (1990). Kale and Upadhye (2003) estimated the chlorophylle contents and inorganic constituents of dimorphic ferns namely, *Bolbitis appendiculata*, *Gymnopteris contaminoides*, *Ceratopteris thalictroides* and *Drynaria quercifolia* grown in different habitats of Western Ghats. Kale and Dongare (2007) analysed total nitrogen, crude proteins and nitrate reductase from *Bolbitis appendiculata*, *Bolbitis virens*, *Osmunda regalis*, *Ceratopteris thalictroides* and *Drynaria quercifolia*.

Tectaria paradoxa, *T. wightii*, *T. coadunata*, *Lastreopsis tenera*, *Polystichum harpophyllum*, *P. piceopaleaceum*, *P. moluscense*, *P. squarrosum*, *Arachniodes tripinnata*, *A. aristata*, *A. amabilis*, *Dryopteris hirtipes*, *D. madrasensis*, *D. cochleata*, *D. sparsa*, *D. approximata* chlorophyll, carotenoids, anthocyanin, flavonoids, sugar, reducing sugar, starch, amino acids, phenols, lipids and proline contents are determined (Joseph 1997). In line with the pigments, primary metabolites and secondary metabolites of *Pteris vittata*, *P. multiaurita*, *P. pellucida*, *P. cretica*, *P. scabripes*, *P. biaurita*, *P. kleiniana*, *P. aspericaulis*, *P. mertensoides*, *P. otaria*, *P. argyraea*, *P. linearis*, *P. confusa* and *Acrostichum aureum* are estimated (Jesudass 1997). Patric Raja (1997) validated the quantitative presence of chlorophyll, carotenoids, anthocyanin, flavonoids, sugar, reducing sugar, starch, amino acids, phenols, lipids and proline in *Histiopteris incisa*, *Hypolepis glandulifera*, *Odontosoria chinensis*, *Nephrolepis auriculata*, *N. multiflora*, *Trichomanes obscurum*, *Dicranopteris linearis* var. *sebastiana*, *D. linearis* var. *tenuis*, *D. linearis* var. *brevis*, *Blechnum orientale*, *B. occidentale*, *Cyathea crinita*, *C. nilgirensis*, *Osmunda regalis*, *Pteridium aquilinum*, *Leptochilus decurrens* and *L. decurrens* f. *lanceolatus.* Antonisamy (1997) determined the total contents of pigments and the primary and secondary metabolites in *Dryoathyrium boryanum*, *Athyrium puncticaule*, *A. solenopteris*, *A. lanceum*, *Deparia petersenii*, *Diplazium muricatum*, *D. sylvaticum*, *D. dilatatum*, *D. travancoricum*, *D. polypodioides*, *D. esculentum* and *D. brachylobum*.

Numerous reports were recorded in the quantification of primary and secondary metabolites of Indian ferns, viz. *Christella* spp. (Paulraj et al. 2011), *Selaginella intermedia*, *S. tenera*, *S. involvens*, *S. inaequalifolia* (Sivaraman et al. 2013), *Asplenium aethiopicum* (Johnson et al. 2014a, b), *Dryopteris cochleata* (Kathirvel et al. 2014), *Pteris vittata* (Kaur et al. 2014), *Marsilea quadrifolia* (Sivagurunathan and Xavier Innocent 2014), *Actiniopteris radiata*, *Acrostichum aureum*, *Dryopteris cochleata*, *Drynaria quercifolia*, *Hemionitis arifolia* and *Pityrogramma calomelanos* (Kalpanadevi et al. 2014), *Cheilanthes farinosa*, *C. anceps*, *C. tenuifolia* and *C. albomarginata* (Ghorpade et al. 2015), *Actiniopteris radiata* (Pratima et al. 2015), *Salvinia auriculata* (Suvarnalatha Devi et al. 2015),

Dicranopteris linearis and *Blechnum orientale* (Kalpanadevi et al. 2016), *Salvinia molesta* (Nithya et al. 2015), *Cyathea nilgirensis*, *C. gigantea* and *C. crinita* (Janakiraman and Johnson 2015), *Cheilanthes tenuifolia* and *Asplenium nidus* (Jarial et al. 2018), *Azolla pinnata* (Thiripurasundari and Padmini 2018), *Tectaria cicutaria* (Preeti and Namdeo 2018), *Asplenium indicum*, *Lepisorus nudus*, *Microsorum membranaceum* (Damaynati et al. 2019), *Tectaria coadunata* (Shrestha et al. 2019), *Sphaerostephanos unitus* (Johnson et al. 2020b, b, c), *Dicranopteris linearis* (Zakaria et al. 2020), *Tectaria paradoxa* (Manivannan et al. 2020), *Bolbitis appendiculata* (Manivannan et al. 2021), *Selaginella repanda* (Adnan et al. 2021), *A. caudatum*, *A. hispidulum*, *A. raddianum*, *Anemia wightiana*, *Arachniodes aristata*, *Asplenium aethiopicum*, *A. auritum*, *A. inaequilaterale*, *A. indicum*, *A. laciniatum*, *A. nidus*, *A. nitidum*, *A. polyodon* var. *bipinnatum*, *Athyrium solenopteris*, *Botrychium daucifolium*, *Cyathea nilgirensis*, *Dicranopteris linearis* var. *sebastiana*, *Diplazium cognatum*, *D. esculentum*, *Doryopteris concolor*, *Dryopteris cochleata*, *D. sparsa*, *Hymenophyllum javanicum*, *Hypolepis glandulifera*, *Lastreopsis tenera*, *Lepisorus nudus*, *Leptochilus decurrens*, *Lycopodiella cernua*, *Nephrolepis cordifolia*, *Odontosoria tenuifolia*, *Parahemionitis cordata*, *Phanerophlebia caryotidea* var. *micropteris*, *Pityrogramma austroamericana*, *Pteris linearis*, *P. confusa*, *P. vittata*, *Pyrrosia lanceolata*, *Pyrrosia porosa* var. *porosa*, *Selaginella wightii*, *Thelypteris caudipinna*, *T. meeboldii*, *T. ochthodes* and *T. papilio* (Johnson et al. 2021).

Patric Raja et al. (1992), De Britto et al. (1994), Antonisamy (1997), Joseph (1997) and Jesudass (1997) revealed the relationship between photosynthetic pigments and habitat of the fern. They observed high amount of chlorophylls in the shade- loving ferns followed by partially exposed ferns. Contrary to the chlorophyll content, carotenoid, anthocyanin and flavonoid contents are more in many of the species exposed to sunlight than shaded species. The reduction in the amount of total chlorophylls in the sunlight -exposed ferns may be due to stress that prevailed in the habitat. Antonisamy (1997) observed the flavonoids and anthocyanins in high altitude ferns. Similar findings were reported by Rathore and Sharma (1991) and Patric Raja et al. (1992). High content of flavonoids is a natural protector from the UV rays. Anthocyanin and flavonoid contents are found to be higher in the ferns of high altitude than in the ferns of low altitude (Patric Raja 1997). Variation is not only observed in the phytochemical content based on the habitat, but also the vegetative fronds and fertile ones showed the variation (Vyas and Sharma 1988; Rathore and Sharma 1990; Malik and Bhardwaja 1992; Patric Raja et al. 1992; De Britto et al. 1994; Antonisamy 1997; Joseph 1997; Jesudass 1997). The vegetative frond of ferns possesses more amounts of carbohydrates and sugars than fertile fronds. Varma (1992) observed fewer amounts of total soluble sugars in sporophylls of *Asplenium* than vegetative leaves. Ramachandran et al. (1991) and Antonisamy (1997) observed the variation of starch content in the rhizome and fronds of ferns. They observed more amount of starch in rhizome than aerial portions. In contrary, De Britto et al. (1994) observed more sugar contents in the fronds than the rhizomes, and reverse situation was observed with reference to starch. Beri and Bir (1995) observed

the variations in the reserve food materials among the ferns growing in partial sun / shade or growing in open sun and deep forest shade.

The large quantity of soluble sugars is providing cytoplasmic osmoticum during conditions of intracellular potential and adverse conditions, viz. desiccation (Yadav 1992). Antonisamy (1997) and Jesudass (1997) noted that the ferns growing on sunlight- exposed area possess more amounts of total free amino acids than shade -loving fern. Rathore and Sharma (1990), Antonisamy et al. (1992), Joseph et al. (1993) and De Britto et al. (1994) correlated the concentrations of amino acids, proline, phenolics and lipids with reference to the habitats of the species. Wang De qun (1988) observed the existence of different types of flavonoids in ferns and alkaloids in microphyllous pteridophytes (mostly fern allies). In addition, the presence of phenols, steroids, triterpenoids and tannins is also observed in ferns (Antonisamy et al. 1992; Joseph et al. 1993; De Britto et al. 1994; Johnson et al. 2020b, b, c). Vyas et al. (1989) observed that soft and herbaceous lamina possesses more total phenolics than coriaceous lamina. Jesudass (1997) stated that the variations in the chemical constituents are due to nature of the soil, age of the plant and seasonal and climatic changes.

19.8 Bioactive Principles Isolated from Indian Pteridophytes

Patric Raja (1997) identified and isolated the following flavonoids, viz. flavonol-3-0-glycosides, afzelin and quercitrin from *Dicranopteris linearis* var. *brevis* (Fig. 19.4). Patric Raja (1997) confirmed the presence of quercitrin and isoquercitrin from *Dicranopteris linearis* var. *tenuis* (Fig. 19.4). *Dicranopteris linearis* var. *sebastiana* showed the presence of astragalin, isoquercitrin, rutin and kaempferol-3-O-(4-O-pcoumaroyl-3-O-a-L-rhamnopyranosyl)-a-L-rhamnopyranosyl (1→6)-13-glycopyranoside (Patric raja 1997; Fig. 19.4). Antonisamy (1997) isolated and identified the luteolin glucoside, kaempferol-3-O-glucoside, kaempferol-3-O-diglucoside, quercetin-3-O-glucoside, quercetin-3-O-diglucoside and quercetin-3-O-diglucoside3′-O-xyloside existence from *Athyrium solenopteris*. Luteolin7-O-β-D-glucoside and kaempferol −3-O-β-D-glucoside are isolated and identified from *Pteris confusa* (Jesudass 1997). The flavonoids orientin, isoorientin, vitexin, isovitexin and rutin are isolated from the fronds of *Tectaria paradoxa* (Joseph 1997; Fig. 19.4). De Britto et al. (1995) determined the aglycone chirality in dihydroflavonol −3-O-α-L-rhamnosides from Thelypteridaceae members. Narasimhaiah et al. (2012) isolated two new glycosidic compounds, viz. 2-(3,4-O-diglucos cinnamoyl)-4-hydroxyl furan and 1-heptaloyl, 8-hexyl, 3-(O-diglucos), 10-methyl, 9,10-dihydro naphthalene from ethyl acetate extract of *Actiniopteris radiata*.

Pteridophytes produce secondary metabolites not simply to adapt to their environment but also to resist themselves against several environmental stresses and also for the process of co-evolution with various interacting organisms. Pteridophytes have survived from Paleozoic times and come across various environmental and climatic conditions. Due to the adaptability, pteridophytes are expected to synthesize

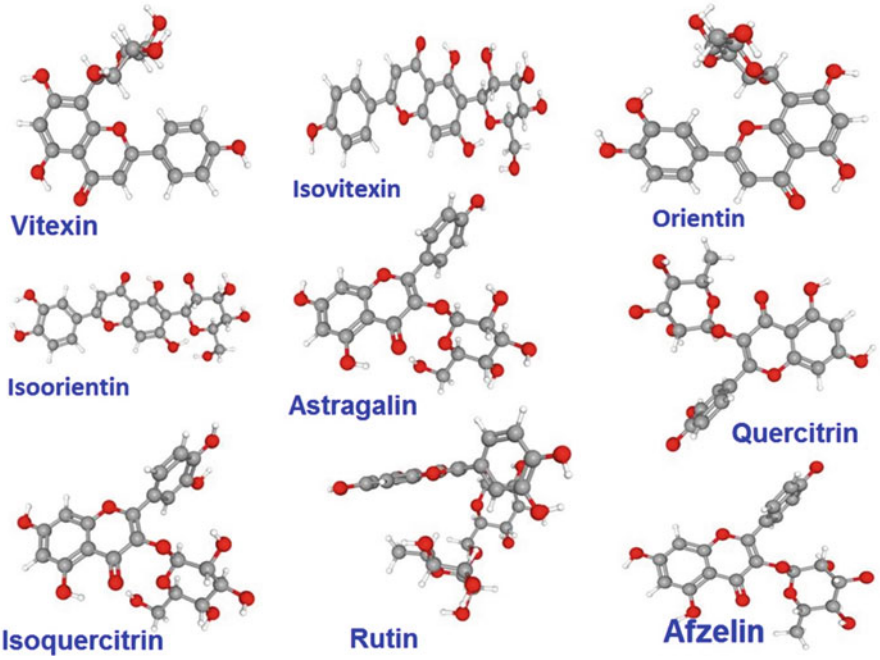

Fig. 19.4 Isolated chemical compound structure of Indian pteridophytes. Source: National Center for Biotechnology Information (2021i). PubChem Compound Summary for CID 5280441, Vitexin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Vitexin. National Center for Biotechnology Information (2021e). PubChem Compound Summary for CID 162350, Isovitexin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Isovitexin. National Center for Biotechnology Information (2021f). PubChem Compound Summary for CID 5281675, Orientin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Orientin. National Center for Biotechnology Information (2021c). PubChem Compound Summary for CID 114776, Isoorientin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Isoorientin. National Center for Biotechnology Information (2021b). PubChem Compound Summary for CID 5282102, Astragalin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Astragalin. National Center for Biotechnology Information (2021a). PubChem Compound Summary for CID 5316673, Afzelin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Afzelin. National Center for Biotechnology Information (2021h). PubChem Compound Summary for CID 5280805, Rutin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Rutin. National Center for Biotechnology Information (2021d). PubChem Compound Summary for CID 5280804, Isoquercitrin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Isoquercitrin. National Center for Biotechnology Information (2021g). PubChem Compound Summary for CID 5280459, Quercitrin. Retrieved July 6, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Quercitrin

and possess many useful secondary metabolites than other land plants. The available literature confirms the existence of many useful phytochemicals (secondary metabolites) such as flavonoids, steroids, alkaloids, phenolics, triterpenoids, amino acids and fatty acids from ferns and fern allies (De Britto et al. 2012a). Due to the existence of these secondary metabolites, the ferns and fern allies harbours various

therapeutical potentials, viz. antioxidant, antibacterial, anti-diabetic, antitumor, anti-fungal, antiseptic, anti-inflammatory activities, etc. (Irudayaraj et al. 2010; Paulraj et al. 2011; De Britto et al. 2012a, b; Sivaraman et al. 2013; Johnson et al. 2014a, b; Janakiraman and Johnson 2015a, b, 2016a, b; Johnson et al. 2017a, b, 2020b, b, c, 2021). The medicinal properties of various plant -derived metabolites are depicted in the Figs. 19.5 and 19.6.

19.9 Medicinal Value of Pteridophytes

The medicinal values of certain ferns in India have been studied (Caius 1935; Nair 1959). Rhizome and roots of *Cheilanthes tenuifolia* are used by the tribal people (Dixit 1959). The young shoots of *Lygodium flexuosum*, a common climbing fern species, is used as vegetable, whereas the rhizome of the plant is boiled with mustard oil and locally applied in scabies, ulcers, rheumatism, sprains, eczema and cuts (Dixit 1959; Dixit and Vohra 1984). *Blechnum orientale* is used as a poultice for boils in Malaya; the rhizome is used as an anthelmintic in China, bladder complaints in India and aromatic in the Philippines (Dixit and Vohra 1984). The rhizome of *Dicranopteris linearis* is used as anthelmintic in Assam while the fronds are used for asthma in Madagascar (Manickam and Irudayaraj 1992). The rhizome of *Pteridium revolutum* (syn. *P. aquilinum*) is astringent, is anthelmintic and is useful in diarrhoea and inflammation of gastric and intestinal mucous membranes. The decoction of rhizome and fronds *Pteridium revolutum* (syn. *P. aquilinum*) is used to control chronic disorders of viscera and spleen. The tender fronds of *P. revolutum* are consumed as vegetables and also employed in soups preparation (Manickam and Irudayaraj 1992).

Drynaria quercifolia rhizome is bitter and used as antibacterial and anti-inflammatory and also for treating constipation, ulcers and other inflammations. The decoction of plant is used in typhoid fever, and fronds are useful in treating swellings (Dixit and Vohra 1984; Warrier et al. 1996). Singh et al. (2001) reported that 14 common pteridophytic species were used by the local people of Manipur. Kirn and Kapathi (2001) observed the ethnomedical uses of 19 pteridophytes in Jammu and Kashmir. Pteridophytes possess various economic values including food, fodder, biofertilizers and insect repellents (Ghosh et al. 2004). Khare and Kumar (2007) studied the ethnobotanical usage of five pteridophytes, viz. *Helminthostachys zeylanica*, *Adiantum philippense*, *Diplazium esculentum*, *Lygodium flexuosum* and *Ophioglossum reticulatum* used by the Tharu tribe of Dudhwa National Park, Lakhimpur, Kheri (Uttar Pradesh). Medicinal values of 61 different ferns and fern allies of the Western Ghats have been prepared by Benjamin and Manickam (2007). Karthik et al. (2011) noticed the medicinal values of 30 pteridophytes from Tamil Nadu. They were used to treat various ailments, viz. wound healing, body sickness, diarrhoea, skin problems, body pain, knee problem, etc. The leaf and root decoction of *Adiantum lunulatum* and *Adiantum philippense* is very effective in the treatment of chest complaints (Rout et al. 2009). The recent ethnobotanical and pharmacological studies confirmed and validated the versatile

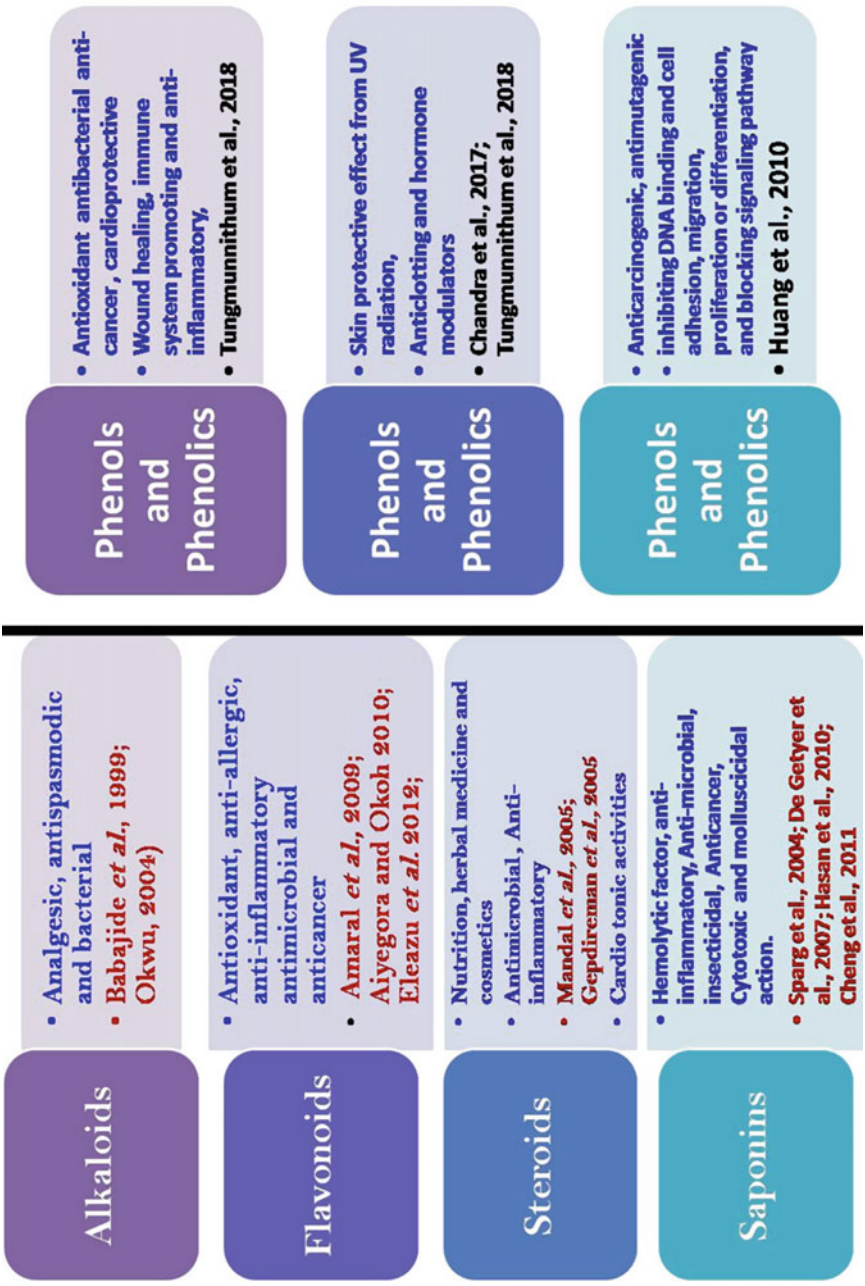

Fig. 19.5 Medicinal properties of alkaloids, flavonoids, steroids, saponins, phenols and phenolics

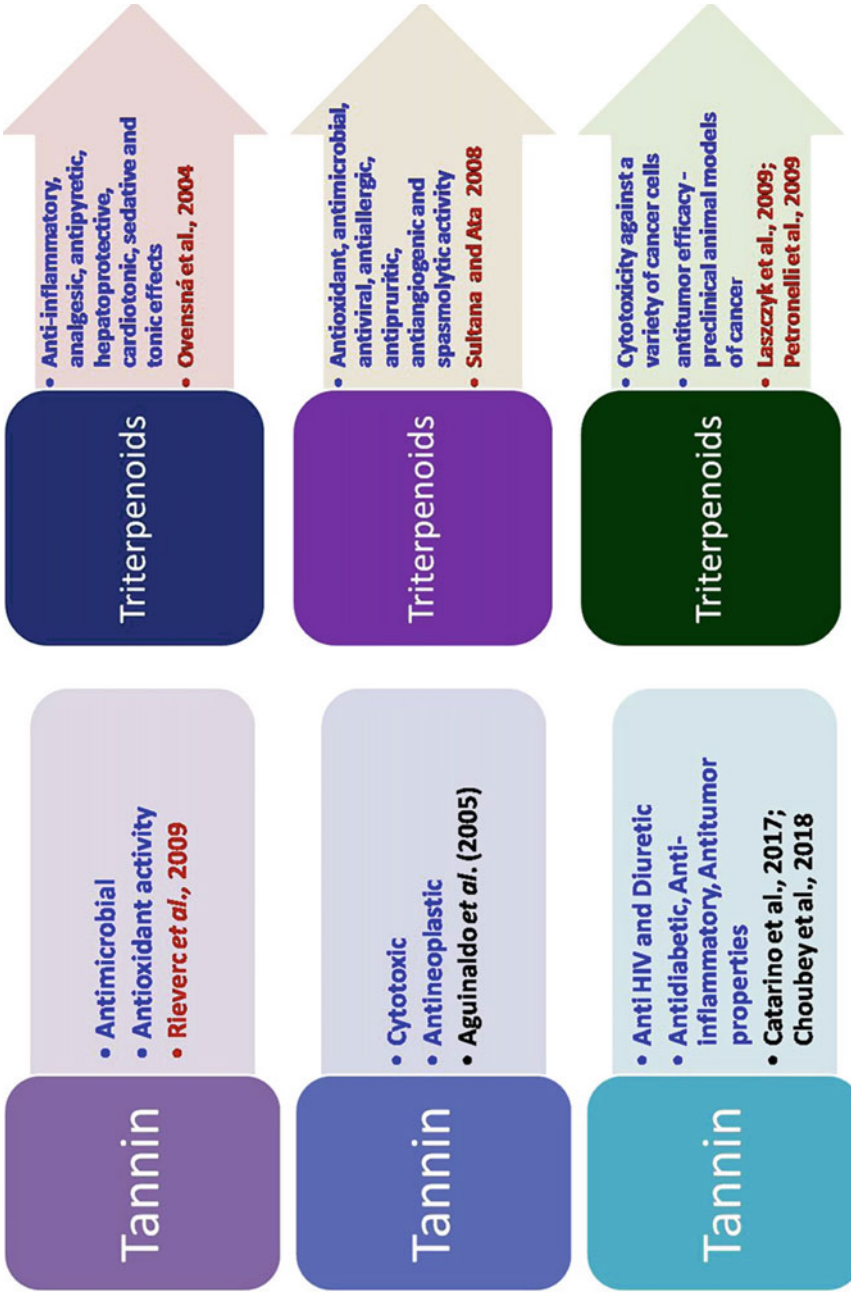

Fig. 19.6 Medicinal properties of tannin and triterpenoids

medicinal application of ferns. The observations and experimental data confirmed the medicinal properties of ferns.

19.10 Conclusion

The available literature on phytochemistry and ethnobotanical and medicinal values confirmed that Indian pteridophytes are a pool of therapeutic agents. A report of 170 species of preliminary phytochemical analysis, quantitative profiles of 115 species, histochemical profiles of 61 species, chromatographic profile (amino acids and sugar) of 43 species, TLC profile of 14 species, HPLC and HPTLC profiles of 23 species and GC-MS profiles of 32 species confirmed the existence of the secondary metabolites, viz. phenolics, tannins, flavonoids, steroids, saponins, triterpenoids, glycosides and alkaloids, in the Indian pteridophytes. The Fig. 19.7 clearly explains the trend of phytochemistry of Indian pteridophytes. Even though a good number of preliminary studies are carried out from Indian pteridophytes, only 21 compounds are isolated and identified so far. Due to the advancement in instrumentation techniques, Indian pteridologists and phytochemists now focussed their attention on quantification of metabolites and isolation and separation of active principles from pteridophytes.

Phytochemical analysis is a very important parameter to identify the new therapeutic source and economically important natural resource. The outcome of the preliminary phytochemical studies on the qualitative and quantitative profiles of Indian pteridophytes revealed the chemical constituents and therapeutic values and provided the chemical marker for the studied species. These profiles will be used as phytochemical markers for the identification of species in the pharmaceutical industries and to find a solution for the taxonomical disputes. Further studies on the isolation and characterization of active principles responsible for the bioactivity are needed.

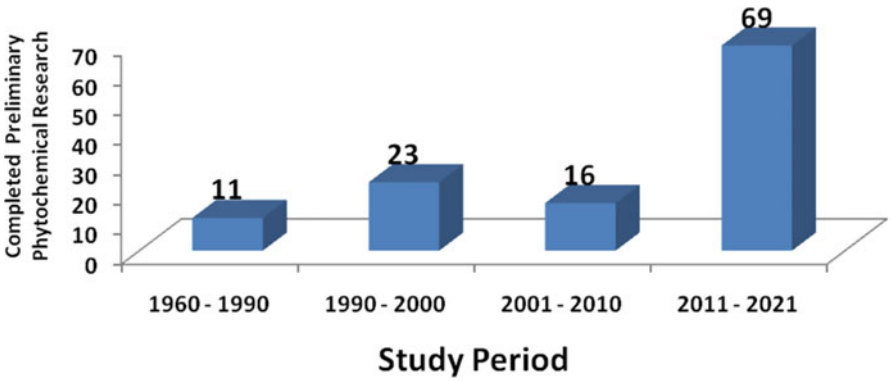

Fig. 19.7 Trend of Indian pteridophytes phytochemistry: preliminary. (Based on the published papers)

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