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HYDROCARBONS AND FATTY ACIDS OF FERNS

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stract—The analysis of hydrocarbons and fatty acids in ten fern species indicate unique differences from plants a higher phylogenetic order. Significant concentrations of fatty acids above C_{20} are present. Distributions of drocarbons range from C_{15}–C_{33} with a trend towards two maxima at C_{17} and C_{29}. Homologous series of ılkenes are present in all species. Pristane and phytane are large components representing up to 27% of the :anes. Distinct alkane and fatty acid differences between fern families are observed while species variations within nilies are slight.

INTRODUCTION

:ns, along with the giant club mosses and giant horse-
.s, were the dominant life form in the Carboniferous
och [1]. Though most of the presently existing species
of relatively recent origin, some families of ferns can
traced to the Devonian Epoch, *ca* 300 million yr ago.
:h ancient lineage suggests that a chemotaxonomic
dy of ferns could be of paleobiological usefulness.
Various classes of compounds have been used in char-
erizing Pteridophytes viz. free sugars [2], polysaccharr-
s [3], pterosins [4], flavonols [5], phenols [6], alka-
ds [7], and triterpenoids [8]. Hydrocarbons and fatty
ds, having been suggested by Shoreland [9] and
eger [10] as suitable candidates for plant chemotax-
omic studies, are also of considerable use in the field
organic geochemistry in establishing ties between
nt lipids and geolipids. Some analyses have been
.de to determine levels of fatty acids in ferns, [11–13]
d the knowledge of hydrocarbons in Pteridophytes has
:ently been advanced. [14–16] Hydrocarbons and fatty
ds in algae, grasses and flowering plants are also well
:umented and bacterial studies include primarily fatty
d analyses. However, few data exist for the Bryophytes
d Pteridophytes.
Several collections of ferns were made to undertake
s study. Three species were collected from the families,
mundaceae and Schizaeaceae, generally accepted to
the most primitive extant families of ferns [1]. Eight
:cies of the family, Polypodiaceae, considered to be
much more recent origin, were collected, two of which
re identical except for place of collection. Of these
species, only *Pteridium aquilinum* has been extensively
/estigated [2,4,17,18]. This particular study was under-
:en to establish and compare the distributions of fatty
ds and hydrocarbons, to investigate phylogenetic rela-
nships of 3 fern families, to assess variations produced
growth locale in the same species and to compare
n lipids with geolipids.

RESULTS

The ten species of ferns show a wide variation of hydrocarbon content ranging from 30 to 416 ppm of the total plant dry wt (Table 1). The fatty acid content in the ferns is less variable (1090–4380 ppm) and is two orders of magnitude greater than the hydrocarbons.

Osmundaceae. The two species examined contain almost identical amounts of fatty acids (*ca* 1700 ppm) and similar hydrocarbon contents (130, 240 ppm). The distribution of hydrocarbons is very similar and shows a smooth distribution of *n*-alkanes between C_{15} and C_{20} with a maximum around C_{17}. There is a significant quantitative difference between the two species in that *Osmunda regalis* contains a larger proportion of high MW hydrocarbons than *O. cinnamomea* (see Table 2). The higher MW alkanes show an odd-carbon number dominance with a maximum at C_{29} for both species. In the range, C_{15-33}, the odd–even ratio of the *n*-alkanes for *O. regalis* is 4.9 and for *O. cinnamomea* 3.8. The isoprenoid alkanes, pristane and phytane, are dominant components in the lower MW region, equivalent in amount to C_{17} and C_{18} alkanes respectively. The percentage of the two isoprenoids in the total saturated hydrocarbon fraction for *O. regalis* is 2.9 whereas for *O. cinnamomea*, it is 13.7.

Fatty acid distributions in both *Osmunda* spp. are almost identical; C_{16}, being the dominant fatty acid followed by $C_{18:1}$ as shown in Table 3. Concentrations in the range C_{21-30} represent 27% of the total fatty acids in *O. regalis* and 28% in *O. cinnamomea*. Two secondary maxima were observed in this range, one at C_{26} and one at C_{30}. In this region the even-carbon number acids occur in concentrations of *ca* ten times those of the odds.

Schizaeaceae. The only representative studied, *Lygodium japonicum*, contains 4 times the amount of fatty acids than the other ferns species, but the hydrocarbon concentration is in the same range as all other ferns analyzed (Table 1). The hydrocarbon distribution is unique

Table 1. Amounts of fatty acids and hydrocarbons in ferns

Family species	μg fatty acids* / g fern dry wt	μg hydrocarbon† / g fern dry wt
Osmundaceae		
Osmunda cinnamonea L.	1770	128
Osmunda regalis var. spectabilis (Wield.) Gray	1740	238
Schizaeaceae		
Lygodium japonicum (Thunberg) Swartz	4380	220
Polypodiaceae		
Polypodium polypodioides (L.) Watt.	1090	349
Adiantum pedatum L.	1300	320
Asplenium sp.	?	246
Pteridium aquilinum (L.) Kuhn	?	30
Dryopteris ludoviciana (Kunze) Small	?	82
Thelypteris hexagonoptera (Michaux) Weatherby	?	416
Polystichum acrostichoides (Michaux) Schott, I‡	?	273
Polystichum acrostichoides (Michaux) Schott, II‡	?	497

* Wt of total fatty acid methyl esters. † Wt of total aliphatic hydrocarbon fraction. ‡ I collected in Tishomingo State Park, II in Vancleave, MS. Note: The phylogenetic arrangement generally follows that of: H. A. Gleason, *The New Britton and Brown Illustrated Flora of the Northeastern United States and Adjacent Canada* Vol. I, Hafner, New York (1968).

in that *n*-alkanes between C_{10} and C_{20} are almost absent but the two major components in this MW range are the isoprenoids, pristane and phytane representing 0.3% of the total saturated alkane fraction. The major alkane is C_{33} representing 83% of the total alkane fraction. There is a strong odd/even carbon number preference between C_{15} and C_{33}, the ratio between the two being 15. A homologous series of *n*-alkanes is also present and exhibits an even-carbon number preference.

Dominant fatty acids in *L. japonicum* are C_{16} and $C_{18:1}$, occurring in similar proportions. Fatty acids between $C_{21\text{-}30}$ represent only 9.5% of the total fatty acids and in this region the even-carbon number fatty acids exceed the odd numbered ones by 16 to 1.

Polypodiaceae. The distribution of hydrocarbons in this group are characterized by the presence of homologous series except in *Adiantum pedatum* and *Pteridium aquilinum* which have alkanes and alkenes distributed in a rather random fashion (see Table 2). Between $C_{15\text{-}33}$, the ratio of odd-numbered alkanes to even averages two for all members of the family. *Polystichum acrostichoides* I has the highest ratio, 4.9 and *P. aquilinum* has the lowest, 0.11. The dominance of odds, however, is not as strong as that found in the Osmundaceae. The amounts of *n*-alkane and *n*-alkenes above C_{20} are 2.8–9 times greater than those of the lower MW in five of the Polypodiaceae. The other 3 species, *A. pedatum*, *Thelypteris hexagonoptera* and *P. acrostichoides* II, have greater amounts of hydrocarbons less than C_{20} (see Table 2). With the exceptions of *A. pedatum* (with maximum $C_{19:1}$) and *P. aquilinum* (with maximum of $C_{32:1}$), the major hydrocarbon is an odd carbon *n*-alkane. In *Asplenium* sp., *T. hexagonoptera* and *P. acrostichoides* II C_{29} is the major hydrocarbon C_{31}, in *D. ludoviciana*, and C_{33} in *P. polypodioides* and *P. acrostichoides* I. Besides *n*-alkanes, a number of *n*-alkenes were noted especially in *D. ludoviciana* and *P. acrostichoides* I and II with a slight dominance of even-carbon chain alkenes.

Pristane was found in all species in this family and phytane, in all but *D. ludoviciana*. These two components occur in equal amounts in all but *D. ludoviciana*, and together they account for 4.1–27% of the total alkane fraction. This concentration range overlaps that of the Osmundaceae, but is far higher than that found for the Schizaeaceae.

The two dominant fatty acids in *P. polypodioides* and *A. pedatum* are C_{16} and $C_{18:2}$ (Table 3). However, a large proportion (*ca* 25%) of the total fatty acids comprises acids greater than C_{21} a figure in agreement with the *Osmunda* and over twice the amount obtained in *L. japonicum*. Among the higher fatty acids C_{24} predominates in *P. polypodioides* and C_{28}, in *A. pedatum*. The even-numbered high-MW fatty acids exceed the odds by at least a factor of 7. This is in contrast to *L. japonicum* whose even numbered fatty acids exceed the odds by a factor of 16.

DISCUSSION

Ferns appear to differ from the higher plants in that they contain a relatively large concentration of low-MW alkanes whose distributions are similar to those of the lower plants, algae and bacteria. Higher plants generally contain hydrocarbons which are 10 to 50% *n*-alkanes, with carbon chains ranging from C_{21} to C_{35} carbon atoms with an odd-carbon preference [19–21]. In many instances one alkane dominates, representing 80 to 90% of the hydrocarbon fraction [21]. More primitive plants such as algae and bacteria contain primarily the lower MW hydrocarbons with C_{17} the maximum of the distribution [22–24]. Hills *et al.* [25] have suggested that the more primitive plant forms may have evolved an alkane distribution which maximizes between *n*-C_{17} and *n*-C_{21} since they were aquatic forms which needed a lower vapor pressure and a solubility suitable for their primitive environment. In a previous study [14], we observed an alkane distribution in the primitive *Lycopodium* spp. similar to the ferns. The normal alkanes fell into two groups, one centred around C_{17} and the other C_{25}, C_{27}, or C_{29}.

Pristane and phytane, the isoprenoid hydrocarbons, occur in relatively high concentrations (up to 27% of the saturated fraction) in the ferns studied. Pristane has

Table 2. Hydrocarbons in ferns. Values in μg hydrocarbon/g fern dry wt

Compound	*O. cinnamomea*	*O. regalis*	*L. japonicum*	*P. polypodioides*	*A. pedatum*	*Asplenium* sp.	*P. aquilinum*	*D. ludoviciana*	*T. hexagonoptera*	*P. acrostichoides* I	*P. acrostichoides* II
C_{15}	0.1	—	—	0.01	—	0.05	—	—	—	0.06	0.04
C_{16}	0.6	—	—	0.2	—	0.2	—	—	—	0.9	0.6
Pristane	1.0	0.07	0.4	0.5	3.0	0.5	0.4	0.2	2.2	1.7	1.8
C_{17}	1.5	0.06	—	0.8	3.5	0.5	0.4	0.1	5.3	3.4	6.0
Phytane	1.1	0.04	0.4	0.9	4.9	0.3	0.4	—	4.4	2.7	5.3
C_{18}	1.1	0.04	—	0.8	5.0	0.2	0.4	0.08	5.6	3.2	7.5
C_{19}	1.7	0.02	0.4	1.0	8.8	0.2	0.9	0.09	8.2	4.3	14.0
$C_{19:1}$	1.0	—	0.3	1.4	15.0	—	0.03	12.0	6.6	22.0	—
C_{20}	0.1	0.03	0.3	0.3	3.7	0.2	0.5	0.06	3.6	1.7	6.0
$C_{20:1}$	—	—	0.1	—	—	—	0.2	0.03	—	—	8.9
C_{21}	—	0.02	0.2	—	—	0.3	0.1	0.1	0.6	—	—
C_{22}	0.05	0.07	0.2		—	0.3	0.2	0.2	0.1	—	—
$C_{22:1}$	—	—	0.2		—	—	—	0.04	0.2	—	—
C_{23}	0.1	0.03	0.2	0.08	—	0.14	0.11	0.08	—	—	—
C_{24}	0.06	0.03	0.2	0.04	0.1	0.1	0.04	0.04	0.2	0.06	—
$C_{24:1}$	0.02	—	0.01	—	—	—	0.02	+	0.03	—	0.03
C_{25}	0.3	0.06	0.4	0.1	—	0.06	0.3	0.05	0.6	0.3	0.5
$C_{25:1}$	0.4	0.02	0.05	0.50	—	0.8	0.1	0.02	0.07	0.1	0.8
C_{26}	0.1	0.03	0.2	0.2	—	0.2	0.07	0.03	0.1	0.1	1.0
$C_{26:1}$	0.02	0.02	0.1	—	—	—	—	0.01	0.1	0.05	0.6
C_{27}	0.6	0.2	0.8	0.9	—	0.2	—	0.1	1.6	0.5	2.9
$C_{27:1}$	0.07	0.3	—	—	7.8	—	—	0.01	—	0.04	—
C_{28}	0.3	0.2	0.6	0.8	—	—	7.9	0.02	0.7	0.2	0.3
$C_{28:1}$	0.3	—	0.7	—	—	—	—	—	—	0.3	0.2
C_{29}	3.6	1.4	5.2	4.2	—	5.2	—	0.2	4.0	1.2	15.0
$C_{29:1}$	—	—	0.4	—	—	—	—	—	—	0.18	—
C_{30}	0.4	0.2	2.3	2.2	1.6	1.6	6.9	0.05	0.3	0.6	0.4
$C_{30:1}$	0.2	—	1.0	—	—	—	—	—	0.5	0.6	0.2
C_{31}	1.0	0.89	22.0	5.2	0.5	0.8	—	0.4	2.4	3.0	2.4
C_{32}	—	+	13.0	5.5	—	—	—	0.05	0.27	2.0	—
$C_{32:1}$	—	—	—	—	—	—	16.0	—	—	1.7	1.1
C_{33}	1.5	0.3	230.0	9.6	6.5	—	—	0.4	3.6	30.0	—
odd/even*	3.8	4.9	15.0	2.2	1.9	2.7	0.1	3.1	2.4	4.9	2.6
HMW/LMW†	1.6	23.0	670.0	9.0	0.71	5.4	7.4	4.8	0.6	2.8	0.7
p + p/sat.‡	13.7	2.9	0.3	4.1	27.0	6.7	4.3	9.0	15.1	7.9	11.1

Cx:y—Hydrocarbon with x carbons + y double bonds. * $\Sigma Cm \div \Sigma Cn$; m is odd, n is even. † HMW = ΣCr, $r > 20$; LMW = ΣCs, $s \leq 20$. ‡ (pristane + phytane)/(total alkanes) × 100%.

been reported in the hydrocarbons of flowering plants while phytane and large concentrations of pristane have been recovered from algal and bacterial lipids [26–29]. Spleenworts, liverworts, and mosses also contain pristane and phytane [30]. It appears that synthesis of both isoprenoids is a characteristic of the Pteridophyta.

Homologous series of *n*-alkenes somewhat shorter in chain length than the *n*-alkane series were also observed in the ferns and represented *ca* 10% of the total hydrocarbon fraction. The even-carbon number homologues were predominant. This is different to that reported for mono-alkenes in algae [27,31], fruits of higher plants [32,33] and bacteria [34].

Fatty acids in the ferns show less variability than do the hydrocarbons. However, they do contain high concentration of acids above C_{20} which represent over 25% of the total fatty acid fraction. This is different from most higher plants which yield only small amounts of fatty acids over C_{20} [35]. We observed considerable amounts of high MW fatty acids in *Lycopodium* spp. [14] but not to the extent found in the ferns.

Various surveys have indicated that distribution of chemical components (e.g. hydrocarbons and fatty acids) in plants may be of limited taxonomic use [36]. It has been pointed out that this limitation is due in part to the distribution dependence of *n*-alkanes and fatty acids on locality, season [37] and morphological plant parts [38]. Our results with *P. acrostichoides* further emphasize the role of locality upon the distribution pattern of *n*-alkanes. *P. acrostichoides* I from Tishomingo State Park has a somewhat higher ratio of odd-C/even-C alkanes than does *P. acrostichoides* II and about the same relative amounts of pristane and phytane. The qualitative distribution is very similar with the exception of a trend towards enrichment of high MW hydrocarbons in *P. acrostichoides* I. Actual gas chromatograms of the two specimens reveal more similarity than do the tables, suggesting that some subtle characteristics of hydro-

Table 3. Fatty acids in ferns. Values in μg fatty acid methyl ester/g fern dry wt

Compound	*Osmunda cinnamomea*	*Osmunda regalis*	*Lygodium japonicum*	*Polypodium polypodioides*	*Adiantum pedantum*
C_{10}	0.2	—	0.08	0.3	—
C_{11}	+	—	0.05	0.3	—
C_{12}	0.7	—	1.4	3.5	+
C_{13}	10.08	—	0.4	—	0.02
C_{14}	0.7	0.7	52.2	13.5	0.5
C_{15}	0.6	0.1	12.2	12.9	0.4
C_{16}	48.8*	12.4	1530	521	14.3
C_{17}	0.5	0.2	35.2	15.7	0.8
C_{18}	+	+	+	+	1.0
$C_{18:1}$†	5.9	3.5	1580	411	1.6
$C_{18:2}$	0.3	1.7	727	650	3.3
$C_{18:3}$	—	0.4	285	23.5	—
C_{19}	0.9	0.3	—	—	0.5
C_{20}	0.9	1.4	135	64.5	0.8
C_{21}	0.08	0.2	—	—	0.07
C_{22}	1.2	1.0	225	125	1.3
C_{23}	1.6	0.3	15.5	44.5	0.7
C_{24}	2.2	0.4	96.9	303	2.2
C_{25}	0.3	0.08	4.3	19.8	0.1
C_{26}	1.1	1.8	56.8	25.5	0.7
C_{27}	—	—	6.4	0.7	0.02
C_{28}	2.8	1.0	54.0	10.2	3.5
C_{29}	0.6	0.2	1.7	1.6	0.08
C_{30}	13.5	2.8	4.7	19.4	0.6
$\Sigma Cm^1/\Sigma Cn$	7.9	9.3	15.7	7.2	8.0
$\Sigma Cx^2/\Sigma Cy$	28.0	27.0	9.9	24.0	28.0

* May include some unsat. † Cx:y—fatty acid with x carbons and y double bonds.
[1]m—even > 20C; n—odd > 20C. [2]x > 20C; y ≤ 20C.

carbon distributions may be more amenable to a chemotaxonomic study of ferns than *n*-alkanes.

From proposed phylogenetic relationships [1], the Polypodiaceae are given several possible routes of evolution, either from the Osmundaceae, Schizaeaceae or Gleicheniaceae families. Based on the facts presented here little evidence exists for any links from the Polypodiaceae to the Schizaeaceae. Table 4 summarizes some of the similarities and dissimilarities noted between the three families. Although only one species, *L. japonicum*, was used to represent Schizaeaceae, Bottari *et al.* [16] have reported hydrocarbon characteristics for *L. smithianum* that are very similar i.e. predominantly high MW alkanes. It appears then that few similarities exist between the Polypodiaceae and Schizaeaceae and only minor dissimilarities exist between Polypodiaceae and Osmundaceae. Still these three families exhibit sufficient variations in hydrocarbons and fatty acids to enable them to be distinguished; greater care must be exercised, however, in attempting species classification based on these same types of criteria.

Table 4. Prominent features of fern hydrocarbons and fatty acids

Alkane parameters*	Osmundaceae	Schizaeaceae	Polypodiaceae
n-alkanes ($n > 20$) / *n*-alkanes ($n \leq 20$)	> 1	⩾ 1	> 1
n-alkanes (even *n*) / *n*-alkanes (odd *n*)	~ 4	15	~ 2
pristane + phytane / alkanes	⩾ 1	< 1	⩾ 1
Fatty acid parameters*			
% *n*-fatty acids ($n > 20$) of total fatty acids	~ 25	~ 10	~ 25
n-fatty acids (even *n*) / *n*-fatty acids (odd *n*)	~ 8	~ 16	~ 8

* The values presented here represent averages for all species analyzed.

More important perhaps than the taxonomic value of hydrocarbons and fatty acids in ferns is their organic geochemical significance. Isoprenoid alkanes are major components in coal [39], petroleum [40] and oil shale [41] extracts. These compounds are often suggested to be diagenetic products of chlorophyll [40] or other plant constituents [42]; another probable source might have been that which was synthesized by the ferns and related plants existing in ancient times. Fatty acids are found in high concentrations and hydrocarbons in relatively low concentrations in all living matter. On the other hand, the opposite is true for these old organic-rich deposits i.e. alkanes, high; fatty acids, low. One possible explanation of this phenomenon is simple degradation of fatty acids to hydrocarbons [43,44]. However, the supposed lack of high-MW fatty acid materials in plants has made the occurrence of high-MW hydrocarbons more problematic. Most likely the ancient Pteridophytes contained as much high MW fatty acids as did the ten ferns studied providing precursor materials of these high MW hydrocarbons. Thus in addition to filling the void of chemical characterization between the phylogenetically more advanced and less advanced plant species, the ferns could serve as a key to further interpretation of geologically preserved lipids.

EXPERIMENTAL

Whole sporophytic ferns were collected from their natural habitats. *Lygodium japonicum*, *Osmunda regalis*, *Osmunda cinnamomea*, *Dryopteris ludoviciana*, and *Pteridium aquilinum* were taken from Magnolia State Park in Ocean Springs, Mississippi during July and August, 1971. *Polystichum acrostichoides* was sampled in both Vancleave, Mississippi and in Tishomingo State Park near Tupelo, Mississippi during July and September, 1971. The remaining fern species were collected at Tishomingo State Park in September, 1971. 50 specimens of each plant was washed with dist H_2O and allowed to air dry. They were then oven dried at 50°C, pulverized and redried at 60°. Dried material was stored in sterile glass jars until extracted. Herbarium specimens were given to the Botany Section at the Gulf Coast Research Laboratory and identifications were made by Dr. Lionel Eleuterius.

Separation and analysis of lipids. Samples (10–25 g dry wt) were placed in pre-extracted Soxhlet thimbles and extracted with $CHCl_3$ for 48 hr. All fern samples included sporangia except *Thelypteris hexagonoptera*, *Pteridium aquilinum*, and *Polystichum acrostichoides*, collected in Vancleave. The lipid extract was washed 2× with slightly acidic H_2O to remove proteinaceous material and then reduced to a known vol and an aliquot taken for lipid wt analysis. The remainder was evaporated to dryness and the residue refluxed with 0.5 N KOH in MeOH for 18 hr. The alkali insoluble portion was extracted with C_6H_6 and reduced to near dryness, transferred to hexane and placed on top of a glass column filled with Si gel–Al_2O_3, 1:1 Activity grade I. Hexane eluted aliphatic hydrocarbons and mono-olefins. The alkali soluble portion of the lipids was acidified and extracted with C_6H_6. The C_6H_6 extract was taken to dryness and esterified with BF_3 in MeOH under reflux for 1 hr. The fatty acid methyl esters were extracted with C_6H_6 from the reflux mixture, dried and transferred in hexane to a Si gel–Al_2O_3 column. After removing residual hydrocarbons with a hexane wash, the column was eluted with C_6H_6 to give the fatty acid methyl esters.

GLC. Hydrocarbons and fatty acid methyl esters were analyzed on two phases, 3% FFAP on Anakrom Q and 3% SE-30 also on Anakrom Q packed in 1 m × 3.2 mm (o.d.) stainless steel columns. FFAP was programmed from 90–225° at 4°/min with final hold and SE-30 from 100–250° at 4°/min with final hold. GLC response factors were computed on a series of *n*-alkane, *n*-alkene, isoprenoid and saturated and unsaturated fatty acid standards and used to convert peak area to μg/g fern dry wt. Identifications were made by comparison of R_t with authentic hydrocarbon and fatty acid standards.

Urea adductions. An aliquot of all hydrocarbon fractions in C_6H_6 was added to hot MeOH satd with urea. Urea crystals containing normal and terminally branched hydrocarbons were separated from more highly branched components by filtration. The urea adducted hydrocarbons were isolated after destruction of the urea crystals with H_2O and extraction with C_6H_6.

Hydrogenation. Δ-Alkenes were further characterized by hydrogenating an aliquot of all hydrocarbon fractions with H_2 bubbled through a sample in hexane using Adams Catalyst (PtO_2) and by noting any shift in GLC R_t by comparison with those of *n*-alkanes. The degree of unsaturation of fatty acids was also determined after hydrogenation and GLC.

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