Phytochemistry, 1967, Vol. 6, pp. 391 to 398. Pergamon Press Ltd. Printed in England

THE TAXONOMIC DISTRIBUTION OF SOME HYDROCARBONS IN GYMNOSPERMS

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(*Received* 30 *July* 1966)

Abstract—The alkanes of thirty-two Podocarpaceae and other related species have been analysed by gas–liquid chromatography and their taxonomic significance is discussed.

INTRODUCTION

THE use of chemical constituents of plants as an aid to their classification is now a familiar concept—the outstanding example being the work of Erdtman.[1] Chemotaxonomy has been applied mainly to one class of chemical constituent at a time, i.e. the occurrence of alkaloids in Liliaceae plants,[2] of acetylenic compounds in Umbelliferae plants.[3] A number of quantitative, gas–liquid chromatographic studies of the alkane components of the plant waxes have recently been reported[4–6] and it was felt to be of interest to compare the results of botanical classification with those of two chemotaxonomic approaches.

The New Zealand species of Podocarpaceae contain diterpene hydrocarbons—often in considerable amounts—which have been studied by Cambie and his co-workers[7] with a view to their taxonomic distribution. The alkane constituents of these gymnosperm waxes have now been analysed and their use as a taxonomic guide and their relationship with the diterpenes are reported here.

RESULTS AND DISCUSSION

The results of the analyses of the alkanes of the gymnosperms (more than half have been examined previously for diterpenes[7]) are given in Table 1. The waxes—extracted from the plant as in the previous work[7]—were chromatographed on an alumina column to give the hydrocarbon fraction which is a mixture of alkanes and diterpenes. Cambie studied these hydrocarbons in the C_{20} region by isothermal gas–liquid chromatography at 140° on a 1% E 301 column. The present work—using a 1% E 301 column programmed from 100–270° —analysed all hydrocarbons of chain lengths C_{15}–C_{37}. It was thus possible to obtain peaks

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TABLE 1. DISTRIBUTION IN PERCENTAGE WEIGHT OF HYDROCARBONS

Taxon	No.	C_{23} iso	C_{23} n	C_{24} iso	C_{24} n	C_{25} iso	C_{25} n	C_{26} iso	C_{26} n	C_{27} iso	C_{27} n	C_{28} iso	C_{28} n	C_{29} iso	C_{29} n	C_{30} iso	C_{30} n	C_{31} iso	C_{31} n	C_{32} iso	C_{32} n	C_{33} iso	C_{33} n	C_{34} iso	C_{34} n	C_{35} iso	C_{35} n	C_{36} iso	C_{36} n	C_{37} iso	C_{37} n
Podocarpaceae																															
Podocarpus																															
Sect. *Afrocarpus*†																															
P. falcatus	1		0 3		0 5		0·8		0·7		1·6		1·6		46 3		4 1		40·1		0·7		3 3								
*P. gracilior**	2		1·3		1·3		1·6		1·9		3·2		2·5		42·1		5·2		35·6		1·3		3·9								
Sect. *Dacrycarpus*																															
*P. dacrydioides**	3		7·4	T	8 8	T	9·3	T	7·5	T	10·7	T	5·3	T	21 3	T	3 8	T	16 4		1 5	T	5·9		0 7		1 3				
Sect. *Eupodocarpus* A																															
P. henkelii	4										4·8		1·5		49·1		3·0		36·7		1·1		3·7								
P. latifolius	5		1 5		0 7		2·9		1·1		7·0		2·2		39·8		2·9		38 2		1·1		2·6								
P. milanjianus	6		1·4		1 2		1·4		1·4		2·5		2·1		43·6		3·2		34·4		1·0		5 2		0·4		2·1				
Sect. *Eupodocarpus* B																															
P. elatus	7				0·8		0·8		0·8		2·3		1·6		24 6		4·2		54 0		2·6		8 3								
P. macrophyllus	8	T	1 5	T	2·5	T	7·1	T	4·8	T	12·5		6 1	T	19·0		7 1		23 0		4·3		8 8		1·4		1·9				
Sect. *Eupodocarpus* C																															
P. salignus	9		2·7		1·6		2·7		1·6		7·6		2·1		49 5		2 7		26 2		1 0		2·1								
Sect. *Eupodocarpus* D																															
P. acutifolius	10		0·5		0·5		1·6		1·3		13·7		2·4		41·4		4·0		32·1		0·8		1·6								
P. alpinus	11			T	2·0	T	1·5	T	0·7	T	16·7	T	1·7	T	54·6	T	2·2		19 4		0 5		0 7								
P. hallii	12				2·3		2·3		0·9		8·3		2 3		23 4		4·1		53·5		0·9		1·8								
P. nivalis	13				5·2		2·2		1·5		8·9		2 9		45 8		4·5		25·7		1·1		2·2								
P. nubigenus	14				2·2		2·2		1·7		14·0		3·0		31·1		4·4		37 1		1·1		2·2		0·8		0·3				
P. totara	15		0·7		1·3		2·0		2 4		6·5		4·1		29 2		7·2		37·1		2·4		5·0		1·3		0·7				
Sect. *Nageia*																															
*P. nagi**	16		2·3		9·0		4·5		4·1	T	9·8	T	6·4	T	17·3	T	8·3	T	31·2		2·6		3·0		0·7		0·7				
Sect. *Stachycarpus*																															
*P. andinus**	17	T	4 2	T	5·9	T	6·3	T	6·3	T	6·5	T	5·1	T	17·5	T	6 1		35 4		2 3	T	3·9		0 2	T	0·2	T		T	
*P. lawrencei**	18	T	4·1	T	4·6	T	4·6	T	4·1	T	6·1	T	3·1	T	9·8		3 1		34·5		5·6		18·8		1·0		0 5				
P. montanus	19		1·8		6·4		2·8		1·8		5·5		1·8		32·9		6·4		35·8		1·8		2·8								
*P. spicatus**	20[a]		1·4		1 6	T	2·9	T	2·1	T	7·6	T	2 9	T	34 9	T	6·5		28·4		2·3		7·4		0·6		0·6				
P. standleyensis	21						0·4		0·4		2·7		1 1		66·1		3·1		24·4		0·4		1·5								
P. minor	53	0 7	16·8	0·9	7 5		2·5	0 7	3·2		11·3		8·6		24 5		5·9	2·5	12·0		1 3		1·6								
P. nivalis (heartwood)	13A		3·1		2·9		3·1		2·5		8·6		3·4		38·6		4·9		31·0		0·9		0 9								
Dacrydium																															
*D. bidwillii**	22		9·6		11·1		12·7		12·5	T	16 0	T	8·2	T	11·4	T	3·5	T	6 1	T	1·8	T	2·7		1 0		1·4		0 8		1·1
*D. biforme**	23[b]		6·1		6·5	T	10·8	T	6·3	T	21·1	T	6·3	T	17·3	T	3·1		7 2		1·1	T	1·5		0·5		0 5		0·2		0·5
*D. colensoi**	24[c]		8·8		11·1	T	9·6	T	8 1	T	9·9	T	7 9		10·1	T	5·8		10·5	T	3·5		5·2		2·0		2·0		1·8		1·8
*D. cupressinum**	25		1 9		1·9		2·2		2·2		3 6		3 1		25·5		5 6		45·5		3 6		4 8								
D. "farnellii"	26[d]		7·7		9·8	T	8·9	T	8·6	T	11·6	T	10·1	T	14 2	T	7·3	T	9·8	T	3 4	T	3·7	T	1 8		2·1				
*D. franklinii**	27		1·5		2·0	T	2 6	T	2 4	T	4·4	T	2·6	T	6 5	T	3·3		20 9		5·4		44·0		2·0		2·4				
*D. intermedium**	28[e]		8·6		9·4		9·8	T	8·6	T	10·9	T	7·9		13 9	T	6·0		11·3		2 3		3·0		1·5		1 1		0·7		0 7
D. kirkii	29		10 7		10 0	T	12·1	T	9·5	T	10·5	T	8·5	T	9·0	T	7·1		8·1	T	3·1	T	6·0		2·1		2·1		0 7		0·3
D. laxifolium	30[f]		6·1		4·2		6·3		5·2		8·4		11·2		19·7		6·3		13·8		1 1		1·6		0·6		1·0		0·3		0·9
D. araucaroides	52		0·4		0·4		2·5		2·9		41·6		4 2		36·7		1·1		7·4		0·4		2 4								
Phyllocladus																															
*P. glaucus**	31[g]		0·6		1·7		2 9		0·5		6·3		1·7		7·4		1·7		13·1		2·3		32·8		4 6		18 3		1 2		1·2
*P. trichomanoides**	32[h]		1·2		0·6		1·2		1·2		3·0		0·9		5·5		1·2		7·0		1 8		23·7		5·2		36·1		3·6		7 0
Araucariaceae																															
Agathis																															
*A. australis**	33[i]		0·4		1·2		2·8		0 8		1 2		1·6		5·3		4·1		57 3		6·5		16·3		0·8		0·4				
*A. robusta**	34	T	0·9		1·2		1·8		1·5		4·5		1·8		19·0		3·5		28·0		3·6		26·2		2 4		5 7				

Taxon	No.	C_{23} iso	C_{23} n	C_{24} iso	C_{24} n	C_{25} iso	C_{25} n	C_{26} iso	C_{26} n	C_{27} iso	C_{27} n	C_{28} iso	C_{28} n	C_{29} iso	C_{29} n	C_{30} iso	C_{30} n	C_{31} iso	C_{31} n	C_{32} iso	C_{32} n	C_{33} iso	C_{33} n	C_{34} iso	C_{34} n	C_{35} iso	C_{35} n	C_{36} iso	C_{36} n	C_{37} iso	C_{37} n
Araucaria																															
*A. araucana**	35		3·5		4·0	T	6·0	T	5·4	T	10·9	T	6·4	T	20·6	T	4·4		15·4		2·4	T	17·0		1·1		2·7				
*A. bidwillii**	36		T		6·9		2·3		1·5		2·7		1·9		16·8		3·8		32·6		3·1		21·8		1·5		5·0				
*A. excelsa**	37		3·8		12·8		10·2		10·6		20·2		9·5		15·3		2·5		4·8		1·3		6·5		0·8		1·9				
*A. rulei**	38		2·5		4·8		4·1		1·8		6·6		2·7		39·0		3·7		23·8		1·3		7·7		0·7		1·5				
Cupressaceae																															
Cupressus																															
C. lawsoniana	39		0·4		0·4		0·4		0·4		1·6		0·8		2·9		0·8		4·6		2·1		66·6		5·0		13·8				
C. macrocarpa	40		0·3		0·3		0·3		0·3		0·6		0·3		2·0		0·6		3·6		2·0		67·8		5·7		16·1				
C. sempervirens	41		0·4		0·8		0·8		0·4		1·2		0·8		5·3		0·8	T	10·7		2·5		57·6		4·9		13·6				
Libocedrus																															
L. chilensis	42		0·8		0·8		1·6		0·8		1·0		0·8		2·1		0·8		4·7		2·1		56·5		6·0		22·0				
L. decurvens	43		1·1		0·8		2·2		1·1		8·2		1·5		10·8		0·8		7·1		1·1		42·7		3·0		19·4				
L. plumosa	44				1·1		2·3		0·9		10·2		0·9		3·9		0·3		4·2		0·9		28·0		4·5		41·0		1·1		0·9
Thuya																															
T. plicata	45						0·9		0·7		0·9		0·7		2·8		0·6		1·8		0·6		15·1		3·1		67·0		2·5		3·1
Sciadopityaceae																															
Sciadopitys																															
S. verticillata	46[j]		4·2		6·4		8·4		11·5		19·2		5·7		10·2		2·6		7·8		1·3		3·6		0·8		3·1				
Taxodiaceae																															
Cryptomeria																															
*C. japonica**	47		T		3·4		3·4		2·7		5·8		3·5		13·3		2·8		9·8		1·3		18·4		1·6		32·5		0·5		1·0
Cunninghamia																															
*C. sinensis**	48[k]	T	2·5	T	2·9	T	5·0	T	2·9	T	6·8	T	2·9	T	27·0	T	3·8	4·0	25·0	T	2·5	T	10·0		1·2		2·1				
Taxaceae																															
Torreya																															
*T. Nucifera**	49[l]		7·3	T	6·1	T	9·0	T	7·8	T	18·7		6·7		17·4	T	5·6	T	11·2		2·9	T	4·3		1·0		1·0		0·4		0·3
Cephalotaxaceae																															
Cephalotaxus																															
*C. drupacea**	50		0·4		0·6		1·0		1·2		12·2		4·2		45·2		4·9		25·4		0·8		2·5		0·4		1·1				
Pinaceae																															
Larix																															
L. leptolepsis	51		14·2		3·3		8·2		3·0		7·7		3·7		21·2		4·7		20·7		2·1		8·4		0·8		2·0				

* n-C_{21} and n-C_{22} are also present in these species but their areas have not been included.

† Arranged as in Cambie.[7]

These alkanes are present as trace quantity T.

[a] No. 20 has a peak between C_{24} and C_{25}, 0·6%.

[b] No. 23 has a peak between C_{23} and C_{24}, 0·7%; between C_{24} and C_{25}, 9·5% and after C_{37}, 0·5% and 0·2%.

[c] No. 24 has a peak after C_{37}, 1·8%.

[d] No. 26 has a peak after C_{35}, 0·9%.

[e] No. 28 has peaks between C_{23} and C_{24}, 0·8%; between C_{24} and C_{25}, 1·5%; between C_{26} and C_{27}, 2·3%.

[f] No. 30 has peaks between C_{23} and C_{24}, 11·5%; between C_{32} and C_{33}, 0·9%; and after C_{37}, 0·6%.

[g] No. 31 has a peak between C_{24} and C_{25}, 3·5%.

[h] No. 32 has peaks between C_{24} and C_{25}, 0·3%; between C_{25} and C_{26}, 0·3%.

[i] No. 33 has a peak between C_{24} and C_{25}, 1·2%.

[j] No. 46 has three peaks after C_{35}, 3·1%, 6·3% and 5·7%.

[k] No. 48 has peaks between C_{24} and C_{25}, 0·8%; between C_{25} and C_{26}, 0·4%; and between C_{26} and C_{27}, 0·4%.

[l] No. 49 has a peak after C_{37}, 0·4%.

D. farnellii has now been identified as a putative hybrid between *D. laxifolium* and *D. intermedium*.

due to alkanes as well as to diterpene hydrocarbons and although no height measurements were made for the diterpenes, the relative proportions of alkanes to diterpenes could be estimated. In species No. 1, for example, there was approx. 100% alkane whilst in No. 10 only 30% alkane.

The use of a short (90 cm) column of E 301 permitted rapid analysis but it did not separate *iso*-alkanes from *n*-alkanes unless they were present in greater than 5%, i.e. the separation was purely on a molecular weight basis. Like Jarolimek,[8] who showed that Apiezon L was the best column for separating *iso* and *n*-paraffins, we analysed many species on a 180 cm, 1% Apiezon column. In only No. 48 and No. 53 did the amount of *iso*-alkane exceed 2%. In almost every species analysed in this way, very small amounts of *iso*-alkanes were found. A much more striking difference in the elution behaviour on Apiezon L was evident in the diterpenes. In No. 34, eight peaks on the E 301 column appeared as twelve on Apiezon L and in No. 5, where Cambie noted only kaurene, the Apiezon L column showed the presence of two major components. There were so many components in the region below *n*-C_{22}, often in very small quantities, that it has not been possible to assign them. The alkanes, however, were identified by comparing their retention times with the retention times of standards run on the same day.

The presence of olefins in rose wax was reported by Šorm[9] and he had previously noted that Apiezon L was not a suitable phase for separation of monoolefins and saturated hydrocarbons. In one species, *Araucaria excelsa*, the mono-ene and saturated hydrocarbons were therefore separated by argentous TLC. The saturated alkanes C_{23}–C_{35} were found to be essentially the same as the original C_{23}–C_{35} hydrocarbons and no alkanes other than diterpenes were observed. In view of the widening horizons of the types of compounds present in plant waxes, there is a need for combined services of a number of techniques: argentous thin-layer chromatography to determine unsaturation,[8] hydrogenation, use of Linde sieve to remove *n*-alkanes from branched alkanes,[10,11] use of a mass spectrometer as a detector for a GLC column.[12]

Analyses were carried out from C_{15}–C_{37} hydrocarbons but peak height measurement was applied only to the C_{23}–C_{37} alkanes because in the lower region the alkane peaks become mixed with the diterpenes and were difficult to assign. The main findings for the alkanes are as follows:

(*a*) The major constituent in these waxes is either *n*-C_{29}, C_{31} or C_{33}, which is usual for plant waxes;[13]
(*b*) There are four species where *n*-C_{35} is the major alkane—which is less usual;
(*c*) The *iso*-alkane content of these waxes is small.

In the section Afrocarpus of the genus *Podocarpus*, the two species have alkane distributions which are similar and this agrees with the botanical classification. No. 2 can be distinguished by the presence of a small quantity of four diterpenes whereas the hydrocarbon fraction of No. 1 is composed entirely of alkanes.

Podocarpus dacrydioides in a small section of its own has a very distinctive alkane pattern.

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The remaining *Podocarpus* species have been grouped into sets (in the figure) according to their alkane distribution patterns, which cut across the botanical classifications. There are two major groupings, species No. 1, 2, 4, 6, 9 and 10 and species No. 12, 7, 5, 19, 14 and 15 with species No. 11, 13, 21 and 20, some of which could perhaps be put into the first group. Nos. 4 and 6 in section *Eupodocarpus* A have similar alkane distributions but No. 5 is quite distinct and separate; the original diterpene work showed that the wax of each species had different components. Nos. 7 and 8, which make up the section *Eupodocarpus* B, have completely different alkane patterns and certainly No. 8 cannot be grouped with any other *Podocarpus*.

Nos. 10, 11 and 13 of the section *Eupodocarpus* D could be grouped together but No. 12 is quite different. Even from the diterpene analyses, section *Eupodocarpus* D is not very

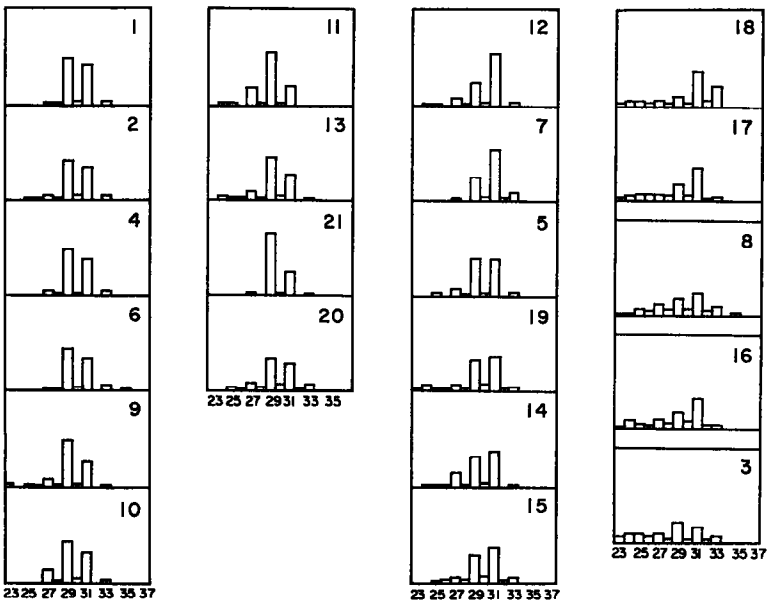

FIG. 1.

homogeneous whilst alkane distributions suggested that it should have two subsections Nos. 10, 11 and 13 in one and Nos. 12, 14 and 15 in another.

Podocarpus nagi, No. 16, also has a singular hydrocarbon distribution.

The next grouping according to the alkane distribution, Nos. 12, 7, 5, 19, 14 and 15, has C_{31} as the major alkane—though the proportion of the diterpene material varies considerably 80, 5, 40, 70, 95 and 80 per cent respectively. According to Cambie's analyses,[7] these species contain widely dissimilar patterns of diterpenes.

The alkane distributions of Nos. 17 and 18 in the section *Stachycarpus* are quite different from those of Nos. 21, 20 and 19. No. 20 has a great deal of low molecular weight material of C number less than C_{15}.

Two of the three remaining species, Nos. 3 and 16 belong to small sections of which they are the only members, however species No. 8 is one member of the Section *Eupodocarpus* B.

In the *Dacrydium* species, the amount of alkane material is often very low and the distribution pattern is strikingly similar to paraffin wax. Where the amount of hydrocarbons

extracted is low or the proportion of alkanes to diterpenes is low the danger of contamination is great and makes any alkane distribution similar to paraffin wax suspect. Only three, Nos. 30, 27 and 25, have alkane patterns which are different and of these Nos. 27 and 25 have 50% alkane material compared with most of the others which have only 5%. It is suspected that No. 26 is a hybrid between *D. laxifolium*, No. 30, and an undetermined species. The alkane distribution pattern of No. 26 is very similar to those of most of the other *Dacrydium* species and not at all like that of No. 30.

Nos. 31 and 32 belonging to the genus *Phyllocladus* have similar alkane patterns and their diterpene constituents are alike.

It is not possible to say that there is any clear-cut difference in alkane distributions between the family Araucariaceae and the family Podocarpaceae. The *Agathis* species Nos. 33 and

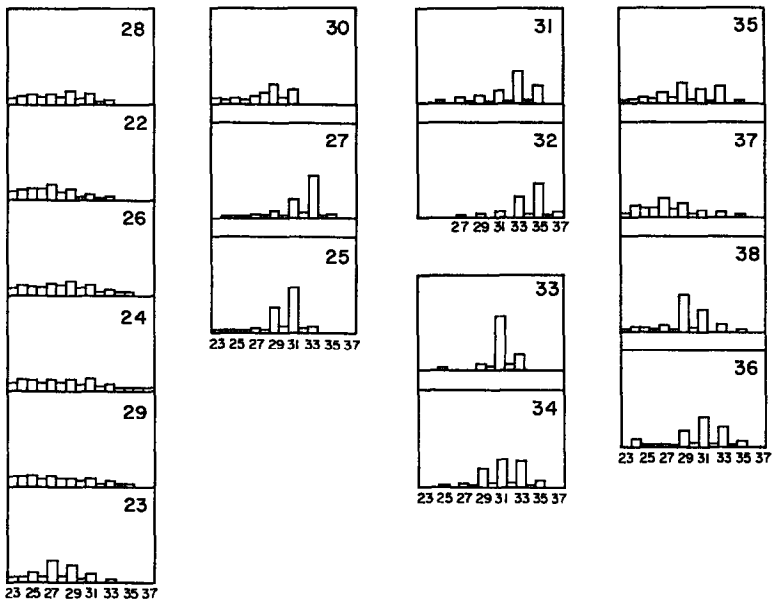

FIG. 2.

34 are surprisingly different in their content of alkanes (15% and 90%), in alkane distribution and diterpene constituents. The four *Araucaria* species each have a separate and distinct alkane pattern, whilst the three which Cambie analysed showed big differences in the diterpenes and in general the Araucariaceae family seems very heterogeneous.

The three *Cupressus* species, Nos. 39, 40 and 41, on the other hand, are very similar in their alkane distribution though their diterpene distributions are by no means identical. The other genera in the Cupressaceae do not have patterns similar to that of the Cupressus. *Thuya plicata*, No. 45, is quite distinct and No. 44 differs from the other *Libocedrus* species.

Each of the remaining species Nos. 46–51 has a distinct alkane pattern though Nos. 48 and 51 have certain similarities.

Cambie reported that species Nos. 1, 2, 7, 9 and 21 contained no diterpenes and in our analyses of these hydrocarbon fractions, they all had less than 5% diterpene material, with the exception of No. 7 with 20%.

In the case of *Podocarpus nivalis*, an extract of the heartwood was made to compare it

with leaf extract. The GLC of the hydrocarbon fraction shows that the alkanes are similar in the heartwood and in the leaf but that there is a high proportion of very low molecular weight material in the heartwood which is absent in the leaf. This feature could be caused by the greater opportunity for volatilization of the lower M.W. material from the leaf.

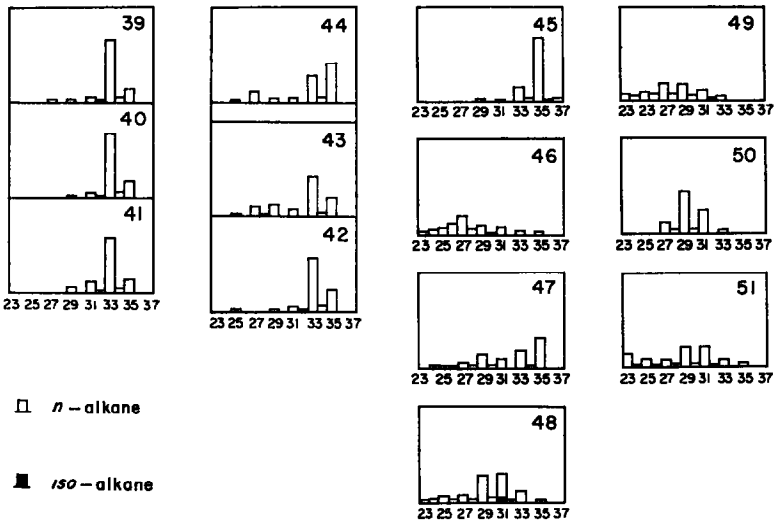

FIG. 3.

CONCLUSIONS

Cambie quoted the example of *Podocarpus spicatus* to show that variation of the diterpene constituents could occur regardless of the geographical location. He went on to suggest that the diterpenes of Podocarpaceae were of little value for taxonomy. The alkane constituents would appear to be a better guide to the botanical classification though there are a number of exceptions. Thus of the twenty-one *Podocarpus* species only three cannot be grouped with the others by their alkane distributions. In a number of species, it was possible to note that both alkane and diterpene contents were unusual—for example, *Libocedrus plumosa* and *Podocarpus latifolius*. It would again appear that the alkane distribution in plant waxes could be used as an aid in taxonomy but would not be sufficiently diagnostic by itself. Even such agreement amongst species of the same genus is all the more surprising in the light of the work on infraspecificity. Barber *et al.*[14] have found that not only does the proportion of hydrocarbon to ketone differ in glaucous and non-glaucous varieties of the same species but the composition of the hydrocarbon fractions also differ.

It has not been possible therefore to combine the diterpene and the alkane results to obtain a more definitive criterion for taxonomy.

EXPERIMENTAL

Species identification and the method of obtaining hydrocarbon fraction are as previously reported.[7]

[14] D. M. HALL, A. I. MATUS, J. A. LAMBERTON and H. N. BARBER, *Australian J. Biol. Sci.* **18**, 323 (1965).

The alkane fraction was analysed by gas–liquid chromatography on a 0·3 × 90 cm column of 1% E 301 on Gas Chrom P (100–120 mesh) using a Perkin Elmer model 800 GLC. The hydrocarbons were eluted by temperature programming from 100–250° whilst the dual column–dual flame ionization detectors maintained base-line stability.

A number of hydrocarbon fractions were analysed on a 0·3 × 180 cm column of 1% Apiezon L.

Weight precentage figures in the table were calculated by measuring peak heights of each peak and using the expression:

$$\text{Weight } \% = \frac{\text{Height}_1}{\text{Height}_1 + \text{Height}_2 + \text{Height}_n}$$

where n is number of peaks in chromatogram.

Acknowledgement. One of us (J. B.) thanks the Fundacion "Juan March" for a research grant.