

Volatile Oils and Plant Taxonomy*

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ABSTRACT—Attempts to utilize the chemical compositions of volatile oils in taxonomy are reviewed. Attention is drawn to the weaknesses in earlier work and some guiding principles to be observed in future work in this field are suggested. Although many promising leads have so far appeared, it is considered that both chemical and botanical data are still too insufficient to enable any conclusions to be drawn.

I

The mid-twentieth century scene in organic chemistry shows a strong interest in what Czapek has conveniently referred to as "secondary plant substances", as distinct from such "primary" plant substances as cellulose and proteins. These secondary plant products—alkaloids, glycosides, flavones, gums, resins, waxes and so on—have provided many interesting problems in the elucidation of molecular structure and stereochemistry, and have brought to light many novel and useful substances. As a natural extension to these studies, there has followed enquiry into biosynthetic mechanisms operative within plants, into speculation on the function of these substances in the plant economy, and finally, as to whether they have taxonomic significance, and it is this last-mentioned enquiry which will concern us here. Although chemotaxonomy has been the subject of two recent monographs (Alston and Turner, 1963; Swain, 1963), neither of these works contains a chapter devoted to essential oils considered as a phytochemical category, and the present paper is therefore supplementary to these volumes, both in dealing with this aspect of the topic, as well as in calling attention to more recent data and thought not available in the works just cited. This omission will doubtless be rectified in the work of Hegnauer (1962-) now appearing.

The examination of the possible value of chemistry to plant taxonomy now dates back some considerable time: indeed, early in the 19th century it was observed that certain families displayed a high frequency of occurrence of certain chemical classes—alkaloids in Solanaceae, oleo-resins in Pinaceae, and so on. This paper deals specifically with volatile or

essential oils, and here again, in this special case of a phytochemical product, it was early observed that the occurrence of volatile oils was not completely random, but characterized certain families such as Labiateae, Rutaceae, and Myrtaceae. Taking these general observations a step further, chemists noted that, as a result of consideration of the various compounds present in volatile oils, there existed the possibility of a relation between oil composition and the systematic position assigned to the plant. One or two examples will suffice to illustrate this kind of indication.

Baker and Smith (1910) observed in the oil steam-distilled from the foliage of *Phyllocladus rhomboidalis* Rich. (Podocarpaceae) the presence of a crystalline diterpene, $C_{20}H_{32}$, named by them phyllocladene (I). Subsequent workers, particularly in New Zealand, reported the presence of phyllocladene or its isomer isophyllocladene (II) in three other species of *Phyllocladus*; and further, that these diterpenes are of frequent occurrence in the leaf oils of *Podocarpus* and *Dacrydium* (also Podocarpaceae), and they have been identified in such related genera as *Araucaria* (Araucariaceae), *Cupressus* and *Libocedrus* (Cupressaceae), *Sciadopitys* (Sciadopityaceae), and *Cryptomeria* (Taxodiaceae) (cf. Aplin, Cambie and Rutledge, 1963). Both phyllocladene and isophyllocladene are unknown in the angiosperms. Again, consider the case of ascaridole (III). This is a most unusual and distinctive compound, being a monoterpene peroxide. It is an explosive liquid and is altogether a substance not to be expected in nature; nevertheless it is found in large percentages in the volatile oil of not only *Chenopodium ambrosioides* var. *anthelminticum* but is present also in the oils of other *Chenopodium* species such as *C. hircinum*.

Following such leads as these, investigators have studied volatile oil compositions from this viewpoint, and some have presented their

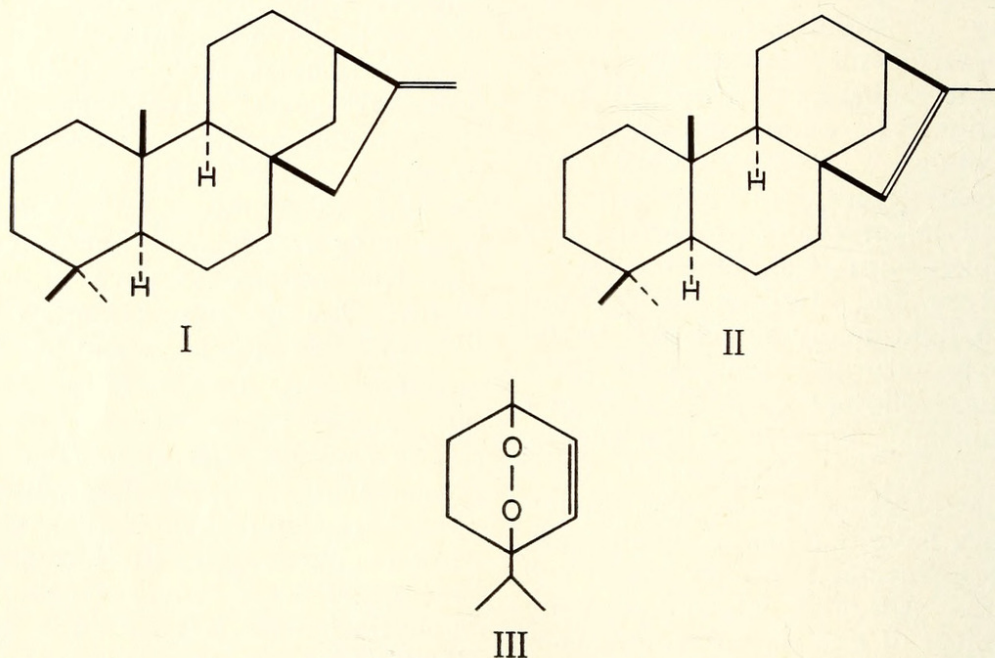
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ideas on the part which chemistry might play in plant classification, and even how it might be applied in phylogeny. Several of these attempts will be briefly examined.

One of the early corpora of work in this field is that of Baker and Smith, who presented their views in two monographs, one on *Eucalyptus* (1920), the other on Australian gymnosperms (1910). Setting aside for reasons of space the work on the gymnosperms, their views on *Eucalyptus* may be summarized as follows: (1) Within the limits of variation typical of living organisms, they regarded the oil composition of a species as constant. (2) They regarded oil composition within the genus as susceptible of classification into major chemical

the intramarginal vein tended to become removed from the margin. With these observations as a starting-point, they postulated an evolutionary pathway in *Eucalyptus*, showing descent from *Angophora*, and how *Eucalyptus* species may have evolved from the more primitive species such as *E. calophylla*.

A second large body of work published in this field is that of Fujita (1951 and subsequent papers), whose monograph sets forth his views on plant classification based on essential oil compositions. Unlike Baker and Smith, who personally accumulated both field and laboratory data on a few genera only, Fujita has theorized not only his own data (e.g. on *Orthodon*), but accepting uncritically published chemical and



groups. Their first group, for example, comprised those oils characterized by the presence of much α -pinene, the absence of α -phellandrene, with 1,8-cineole present in not more than a few per cent. (3) They assumed *Angophora* to be the older genus, and having adduced evidence that *Angophora* oils resembled closely the "pinene group" of *Eucalyptus* oils, they perceived in this a chemical link between *Angophora* and the more primitive eucalypts such as the "bloodwoods" (Series *Corymbosae* and *Corymbosae-peltatae* of Blakely, 1955), all species of which examined by them having been found to yield "pinene oils". (4) They claimed a relationship between oil compositions and leaf-venation; maintaining that pinene oils came from species whose leaves showed transverse parallel venation, the intramarginal vein close to the margin; whilst as phellandrene contents rose, the angles made by the veins with the mid-rib diminished and

taxonomic data (much of it now known to be incomplete or erroneous), has erected on this basis chemical classifications and phylogenies of a large number of genera.

A third work of some magnitude is that of Mirov in *Pinus* (1961). His monograph merits attention for four reasons. Firstly, although much of the work was carried out prior to the advent of gas chromatography, the chemical work is modern and reliable as far as it goes. Secondly, Mirov was at pains to collect botanically authentic material, and was aware of the biological considerations (e.g. hybridism) affecting phytochemical work. Thirdly, he has reported on the compositions of the volatile oils from the oleo-resins of an entire genus. Fourthly, unlike some of the earlier authors, he has preferred to review his data rather than to use them as a basis for elaborate theories.

Such, then, are some examples of the collection of phytochemical data on volatile oils having

as its objective the determination of relationship to taxonomy. Much of the earlier work, however, suffers from certain shortcomings, and that of Baker and Smith in *Eucalyptus* will serve to illustrate some of the errors which must be avoided in researches in this field.

Firstly, chemical data have sometimes been obtained from material from plants of imperfectly-understood or ill-defined systematic position. The genetic complexity of many populations is now familiar: in such cases species limits become blurred, and the chemical data drawn from such populations may become difficult to interpret. Thus, Baker and Smith reported on the oils of many eucalypts now known to be of hybrid origin; for example, *E. vitrea* R.T.Bak. (= *E. pauciflora* Sieber $\times$ *E. dives* Schau. or $\times$ *E. radiata* Sieber ex DC.), *E. irbyi* R.T.Bak. et H.G.Sm. (= *E. dalrympleana* Maiden $\times$ *E. gunnii* Hook f.), *E. unialata* R.T.Bak. et H.G.Sm. (= *E. globulus* Labill. $\times$ *E. viminalis* Labill.) and many others. They further overlooked the complexity in some *Eucalyptus* groups such as Series Psathyroxyla of Blakely (*loc. cit.*), the "scribbly gums", and reference to their herbarium specimens shows that under the name *E. haemastoma* Sm. they included the variety *sclerophylla* Blakely and *E. racemosa* Cav. (syn. *E. micrantha* DC.). Penfold and Morrison (1927b, 1933a) demonstrated great chemical differences not only between *E. haemastoma* and *E. racemosa* but also within *E. racemosa*. Other examples of groups providing genetic difficulty are the *E. mannifera* Mudie group (Johnson, 1962), treated by Baker and Smith in part under *E. maculosa* R.T.Bak., *E. lactea* R.T.Bak., and *E. gullicki* R.T.Bak., and the *E. andrewsii* Maiden-*E. campanulata* R.T.Bak. complex (treated as two distinct species by Baker and Smith).

Secondly, some earlier theories have been based on deficient chemical data: in very many cases Baker and Smith had identified compounds comprising less than 50 per cent. of the oil (e.g. *E. dawsoni* R.T.Bak., *E. nova-anglica* Deane et Maiden, *E. fibrosa* F. Muell. (*in loc. cit.* "*E. siderophloia* Benth.") and *E. eximia* Schau. In the case of only a very few species did these authors have a knowledge of oil compositions accounting for the greater portion of the oil.

Thirdly, if chemical variation within a "good" species occurs, it will present problems in the accommodation of chemical data to a scheme relating them to the systematic position

of a plant. This phenomenon will be referred to later, but at this juncture it may be recalled that Baker and Smith encountered variations in oil composition within a species, and that it caused them great difficulties in their schemes of classification and phylogeny. Their treatment of the phenomenon was inconsistent: in *E. viminalis* they simply admitted the difference, and designated the variant "variety A"; in *E. camaldulensis* Dehnh. (*E. rostrata* *in loc. cit.*) they formally erected the varietal taxon of *borealis* to differentiate those trees yielding an oil rich in cineole, but morphologically inseparable from those of populations earlier encountered, but which yielded a markedly different type of oil. In *E. radiata* Sieber ex DC. (*in loc. cit.* *E. australiana* R.T.Bak. et H.G.Sm., *E. phellandra* R.T.Bak. et H.G.Sm., and *E. amygdalina* var. *nitida* Benth.) separate taxa of specific rank were erected solely on chemical grounds. Finally, in *E. dives* Schau. the observation by these authors of a profound chemical variation (*E. dives* var "C" of Penfold and Morrison, 1927a) was so at variance with their scheme that they rejected these trees as belonging to *E. dives* and referred to them as "*E. australiana* var. *latifolia*".

Finally, attempts to classify plants by chemical groups (as did Baker and Smith in *Eucalyptus*) may be misleading unless an adequate knowledge of oil compositions is available. These workers were compelled to establish a category for species "yielding an oil not readily placed in the other groups". Their theory of correlation of leaf venation with chemical composition of the oils suffered from the existence of this category: *E. citriodora* Hook., for example, with its venation (and all other characters) typical of Series Corymbosae-peltatae of Blakely, failed to yield an oil rich in α -pinene, but was found to contain citronellal as major component. Research continues to demonstrate the existence of species whose leaf oils are of unexpected chemical composition. Sutherland, Webb and Wells (1960), for example, showed the leaf oil of *E. deglupta* Blume from New Guinea to consist largely (c. 50 per cent.) of nerolidol, together with ocimene, α -pinene, α -phellandrene, *p*-cymene, carvatonacetone and isovaleraldehyde; and Hellyer, Keyzer and McKern (1964) have found that the leaf oil of *E. crenulata* Blakely et de Beuzeville consists largely of methyl 3,4,5-trimethoxybenzoate (c. 47 per cent.) and γ -terpinene, accompanied by lesser amounts of *p*-cymene, α -pinene, terpinolene, isovaleraldehyde, and terpen-1-en-4-ol.

The lesson to be learned from this review of earlier work is not only that data must be interpreted more critically, but that the phytochemist must also collect his data more critically against a background of awareness of the biological factors involved. Willis, McKern and Hellyer (1963), for example, suggest the following experimental procedure: (1) Collect chemical data (at least initially) only within well-defined species. (2) Working always on the same organ, compare oils of individual plants within the one population, or from the same site. (3) Compare data from population to population, or from site to site. (4) Test the inheritance of both chemical and morphological characters. This procedure may then with advantage be applied to plants or populations of plants where taxonomic limits are less clear (e.g. between *Pinus halepensis* and *P. brutia*, cf. Mirov, *loc. cit.*, pp. 111, 130–131).

II

The threads of chemical affinity already referred to, and which appear to link taxa already accepted from morphological considerations as related, undoubtedly exist and have received much attention. Not so much prominence, however, appears to have been given to the equally frequent lack of obvious chemical connection between closely-related

taxa. The genus *Backhousia* (fam. Myrtaceae) provides an example. It is a small genus from which only nine species have been described. The genus itself is well separated from other cognate genera within the family, and further, species limits within the genus are sharply defined, so that no taxonomic difficulties are present. Of the nine species known, seven have been examined for their leaf oils; reference to Table I demonstrates the lack amongst these species of an obvious chemical linkage of the sort being discussed.

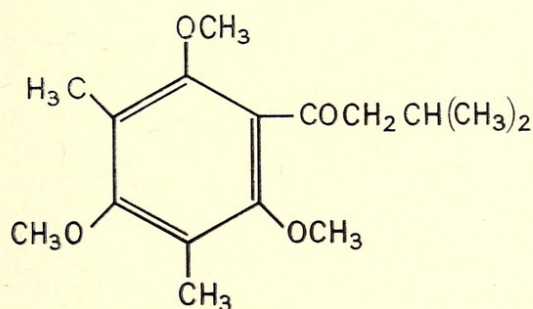
The use of the "unusual" or infrequently-encountered essential oil constituent as a means of tracing affinities amongst plants has already been referred to. Some guidance as to the reliability of this procedure is provided by the work of Bowyer and Jefferies (1959, 1962) on the incidence of torquatone in *Eucalyptus*. This substance was first discovered by these workers in the leaf oils of *E. torquata* J.G. Luehm. and of *E. caesia* Benth., and was shown by them to have the structure IV shown above. Of a further 40 species examined, another two showed the presence of torquatone: *E. flocktoniae* Maiden and *E. spathulata* Hook. var. *grandiflora* Benth. Significant points emerging from this study are: (i) As the authors themselves remark, "the four species found to contain torquatone are considered to have

TABLE I
Leaf Oils of Backhousia Species

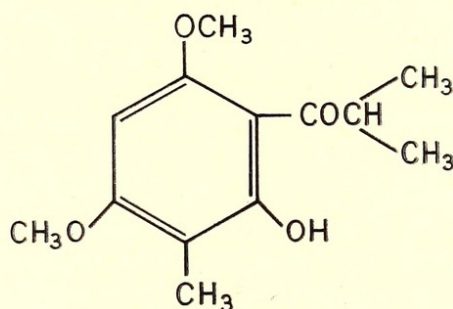
Species	Chief Constituents of Oil	References
<i>B. angustifolia</i> F. Muell.	(a)*Dehydroangustione; angustifolionol. (b) Dehydroangustione. (c) Angustione; angustifolionol.	Cannon and Corbett (1962)
<i>B. anisata</i> Vickery	Anethole	McKern (1949)
<i>B. bancroftii</i> F. M. Bail. et F. Muell.	Chiefly sesquiterpenes and sesquiterpene alcohols; α -pinene; esters.	Lahey and Jones (1938)
<i>B. citriodora</i> F. Muell.	(a) Citral, 90–95 per cent. (b) Citronellal, 62.5–79.7 per cent.; isopulegol; citronellol; esters.	Penfold <i>et al.</i> (1951)
<i>B. hughesii</i> C. T. White	α - and β -pinene; sesquiterpenes and sesquiterpene alcohols.	Jones and Lahey (1937)
<i>B. myrtifolia</i> Hook. f. et Harvey.	(a) Elemicin. (b) Isoelemicin. (c) Eugenol methyl ether. (d) Isoeugenol methyl ether and iso-elemicin.	Penfold (1922); Penfold, McKern and Spies (1953); Hellyer, McKern and Willis (1955).
<i>B. sciadophora</i> F. Muell.	α -pinene, 80–85 per cent.; sesquiterpenes and sesquiterpene alcohols.	Penfold (1924).

* The alternative entries (a), (b), (c) or (d) in the centre column refer to differences in oil composition occasioned by the existence of chemical races or forms within the species.

very little botanical affinity"; *E. caesia* (series Obliquae), *E. spathulata* (series Cornutae) and *E. torquata* (series Dumosae) are widely enough separated within section Macrantherae, but *E. flocktoniae* (series Subulatae of section Platyantherae) is, at least on Blakely's classification, of little affinity with the other three. (ii) The species found by Bowyer and Jefferies not to contain torquatone comprise six from series Dumosae, closely related to *E. torquata*, and another six from series Cornutae and having close botanical affinity with *E. spathulata*.



IV



V

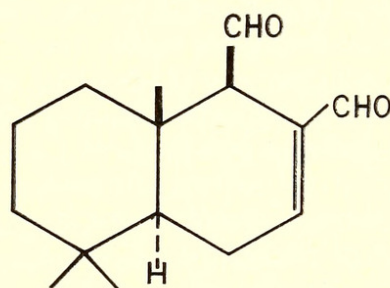
E. griffithsii Maiden is classified as related to *E. caesia*, also in series Obliquae. (iii) Further, gas chromatographic examination of the oil of typical *E. flocktoniae* showed no indication of the presence of torquatone; this substance was detected only in a form having ribbed fruits from the Lake King district of Western Australia. With *E. spathulata* var. *grandiflora*, only one sample (from the large-fruited form from Lake King) yielded an oil containing torquatone.

Another aromatic substance, baeckeol (V), provides a further example of the inconclusive results of following the incidence of the "unusual" compound: discovered first in the leaf oils of *Baeckea imbricata* (Gaertn.) Druce (*B. crenulata* R.Br. in loc. cit.) and of *Darwinia procera* B. Briggs (*D. grandiflora* in loc. cit.) by Penfold (1922b, 1923), the same author (1925) demonstrated its presence in *B. gunniana* Schau. var. *latifolia* F. Muell. (but not observed in *B. gunniana* by Smith (1922)), whilst Spoelstra (1931) later found it in the extra-Australian *B. frutescens* L.; and quite recently Bowyer and Jefferies (1962) have shown it to be a component of the Western Australian *Calytrix angulata* Lindl. Baeckeol is thus seen, from an evolutionary point of view, to be diffused through at least three*

genera of the Myrtaceae extending from south-east Asia to both the eastern and western extremes of the Australian mainland. Investigations on the oils of other *Baeckea*, *Darwinia* and *Calytrix* species have not disclosed the presence of baeckeol (Baker and Smith, 1899; Penfold, 1927; Jones and White, 1930; Penfold and Morrison, 1933b; Penfold, Ramage and Simonsen, 1934; Bick and Jones, 1940; Jones, Lahey and Sutherland, 1949).

In fact, the unusual compound is likely to be found in plants widely separated in botanical

classification. Consider the aromatic ester methyl salicylate: it is not commonly met in large percentages in essential oils, but nevertheless forms the major part of the oil of the angiosperm *Gaultheria procumbens* L. (Ericaceae) and of the botanically remote *Asplenium lamprophyllum* Carse (Aspleniaceae), a pteridophyte (Briggs and Taylor, 1947). Furthermore, these authors record that they failed to detect this



VI

ester in *A. bulbiferum* Forst. f. (almost indistinguishable from *A. lamprophyllum*), in *A. lucidum* Forst. f., in *A. flaccidum* Forst. f., or in *A. falcatum* Lam.

Again, it would appear that sesquiterpene dialdehydes are uncommon plant constituents; nevertheless, the first two reports on a substance of this class, polygodial (VI), are from two widely separated families. Barnes and Loder (1962) first discovered polygodial in the leaves of *Polygonum hydropiper* L. (Polygonaceae)

* And four, if (as seems likely) the yellow crystalline substance of m.p. 104° found by Jones and White (1931) in the leaf oil of *Leptospermum luehmannii* F. M. Bail. (in loc. cit. *Agonis luehmannii* (F. M. Bail.) White et Francis) is baeckeol.

and in the same year Loder (1962) found it in the quite unrelated *Drimys lanceolata* (Poir.) Baill. (Winteraceae).

To sum up, whilst it must be admitted that some sort of a frequency pattern of volatile oil compounds has emerged (for example, the extraordinary frequency of occurrence of α -pinene), nevertheless, the selection of an "unusual" or infrequently encountered compound as a taxonomic tracer is scientifically unsound; its unfamiliarity may be due simply to insufficient investigation. The eudesmols were once thought to be confined to *Eucalyptus*; they are now known to occur in widely separated genera.

Further, not only does it appear that the same compound is likely to be encountered in the oils of unrelated species, but it seems that oils of very similar, if not identical, composition may be produced by plants from different species, genera, or separated by even higher taxonomic categories. McKern (1956) has suggested that, rather than attempt to link oil compositions with taxonomy, it would perhaps be better to think in terms of the biochemical system operative within the plant, on the assumption that this genetically-determined enzyme system results in the elaboration of a certain set of compounds which collectively constitute the oil. Hence it may be possible to recognize groups of oil compositions to one of which the plant may be linked, rather than to attempt to relate the composition of a single oil, or a selected component, to a taxonomic system. Unfortunately, our knowledge of the ultimate compositions of oils is still very far from complete, but there are strong indications that the compositions of oils from a number of different plants may be similar. In *Eucalyptus*, for example, it is not possible in our present state of knowledge, to distinguish qualitatively amongst the oils of the "piperitone form" of *E. andreana* Naud., of *E. dives* Schau., of *E. radiata* Sieber ex DC., of *E. piperita* Sm. or of *E. racemosa* Cav. In such work, care must be taken that artefacts (arising perhaps from the method of isolating the oil) are not confounding factors.

III

The simple correlation of volatile oil composition with the systematic position of a plant is likely to be complicated by the frequently-reported examples of chemical variation within a species. This phenomenon appears to have been observed for most chemical classes of secondary plant products, e.g., in alkaloidal

plants (Steinegger, 1957), in glycosidic plants (Van Os, 1957), and in cyanogenetic plants (Dillemann, 1957), and has been the subject of much useful review and comment (cf. Mothes, 1957; Hegnauer, 1957; Dillemann, 1959). These authors are concerned with the phenomenon of pronounced chemical differences existing between plants or between populations of plants within a species which is otherwise well defined by the usual morphological criteria, and where no morphological character may be seen to be linked with a chemical character. The term "chemical races" has come into use for reference to these variants, which Hegnauer (1957) defines as follows: "In allgemeinen wird man von chemischen Rassen sprechen, wenn man innerhalb einer Species deutliche chemische Differenzierungen beobachten kann, die nicht von erkennbaren (oder erkannten!) morphologischen Differenzierungen begleitet sind." Hegnauer further emphasizes that these taxa are to be regarded as of sub-specific rank.

In the field of volatile oil chemistry, this phenomenon was first clearly perceived by Penfold and Morrison (1927a) as a result of their observations on *E. dives*, and, in the succeeding years their school in Sydney, together with many other workers in other parts of the world, have brought to light a large number of examples. Some of these have been discussed by Stahl (1957) and by Hegnauer (1957), but to emphasize the problem which this phenomenon sets the phytochemical systematist and phylogenist, the examples selected for inclusion in Table II have been chosen because in each instance the variants were observed growing side by side on the same site. The reader is further referred to Table I where, of the seven *Backhousia* species listed, three (*B. angustifolia*, *B. citriodora* and *B. myrtifolia*) are seen to exist in different chemical forms. These examples are of like interest, inasmuch as in the case of each species the chemical variants are also to be found occurring naturally side by side under similar environmental conditions.

At the time of writing, the evidence for chemical races within species showing not only quantitative chemical differences, but also those of a pronouncedly qualitative nature, is both strong and striking. However, the chemical data on which it rests must be regarded as incomplete, inasmuch as no chemist has yet accounted for every constituent of an oil. Even with the use of gas chromatography, perhaps not more than 99 per cent. of an oil has been accounted for, and in the remaining

TABLE II
Chemical Variation Within Some Essential Oil-bearing Species

Species				<i>Melaleuca bracteata</i> F. Muell.		
Chemical variety	..	..	1	2	3	
Major components of oil	..	Eugenol methyl ether.		Isoeugenol methyl ether.		Elemicin.
Reference	..	..	..	Penfold, Morrison, McKern and Willis (1950).		
Species				<i>Melaleuca quinquenervia</i> (Cav.) S. T. Blake		
Chemical variety	..	..	1	2	3	
Major components of oil	..	Nerolidol (ca. 90 per cent.)		Nerolidol and linalool (15-50 per cent.).		α -Pinene, 1,8-cineole, (—)-limonene, α -terpineol, viridiflorol.
Reference	..	..	..	Hellyer and McKern (1955) under <i>M. viridiflora</i> Gaertn.		
Species				<i>Leptospermum liversidgei</i> R. T. Bak.		
Chemical variety	..	..	1	2		
Major components of oil	..	Citral, linalool, α -pinene.		Citronellal, isopulegol, α -pinene.		
Reference	..	..	..	Penfold (1922, 1931) ; McKern (1956)		

1 per cent. may be found compounds whose presence may modify our views. Of the great majority of essential oils whose compositions are reported in the literature, few have had more than a dozen or so components recorded. However, the most recent examinations of essential oils by gas chromatography show that an oil may contain well over 100 components, of which most are present in only minute quantities, perhaps as little as 100 parts per million or less. The application of such refined analytical techniques will undoubtedly shed much light on the nature and extent of chemical variation in essential oils, but much remains to be done. In order to disprove the theory of chemical races (differing qualitatively from each other) in essential oil-bearing plants, a great number of compounds will have to be positively identified in perhaps less than 1 per cent. of the variant oil in order to establish its qualitative identity with the norm.

An instance of progressive refinement of knowledge of chemical variation within a species is provided by the recent work of Gottlieb, Magalhaes and co-workers (1959, 1960, 1962) on physiological forms in *Ocotea pretiosa* (Nees) Mez (Lauraceae) in Brazil. The wood oil of this species had long been considered to consist principally of safrole, but in 1960 these workers announced the

occurrence of a form whose oil contained the unusual constituent, 1-nitro-2-phenylethane, together with much eugenol methyl ether. However, on closer examination of the oils from individual trees they showed (1962) that the oil of the nitrophenylethane form may contain varying amounts of safrole, whilst the safrole form, apparently devoid of nitrophenylethane, may contain eugenol methyl ether. The pattern, however, was further complicated by the detection of camphor in small amounts (1-4 per cent.) in some trees of the safrole form, but not in others.

A re-examination of many of these variant oils is therefore clearly called for; but even should this result in the theory of qualitative variation being abandoned,* the fact of discontinuous variation in the percentage of a single constituent from, say, 1 per cent. in the oil of one plant to 90 per cent. in the oil of an adjoining plant of the same species, both plants occurring naturally on the same site and free to interbreed, is of great genetic interest and economic significance. This is not completely

* In fact, Flück (1963) asserts that "Reports of qualitative variation characterized by the fact that one or more substances are *completely* absent in one or more subdivisions of the taxon, and which is, therefore of interest to chemical taxonomy, should always be regarded with suspicion."

a hypothetical example; it is based on the observations of Hellyer and McKern (1955) on the leaf oils of *Melaleuca quinquenervia* (Cav.) S.T. Blake (*in loc. cit.*, *M. viridiflora* Gaertn.) (*vide* Table II). These authors, working on single trees, observed, *inter alia*, that trees of this species yielding oils consisting almost entirely of nerolidol (*ca.* 90 per cent.) were growing side by side on the same site with other trees of the same species whose oils consisted of a complex mixture (1,8-cineole, viridiflorol, α -pinene, limonene, α -terpineol, etc.), in which nerolidol was not detected. *M. quinquenervia* is an exceedingly well-defined species in the area studied, in fact very distinct from all other members of the genus in New South Wales and shows no hybrid tendencies with other *Melaleuca* species.

IV

Setting aside for the moment the extensive data on chemical races, and assuming a chemical constancy for the species, what appear to be the present prospects of utilizing essential oil compositions in plant systematics? Replies to this question have recently been given by two research groups in this field.

The first opinion is that of Aplin, Cambie and Rutledge, who last year (1963) took up again the lead provided by the presence of phyllocladene and isophyllocladene in the Gymnosperm genera already referred to. Using the more delicate technique of gas chromatography not available to earlier workers, these authors described the results of the examination of the leaf oils of 28 species of the Podocarpaceae and of nine other related Gymnosperms. They examined carefully the incidence of the diterpene hydrocarbons phyllocladene, isophyllocladene, kaurene, isokaurene, rimuene and cupressene. After tabulating and considering their data, they came to the following conclusion: "It would appear from the present survey that the diterpene hydrocarbons are of doubtful taxonomic value. From the observation that these compounds were absent in five species distributed over three of the sub-sections of the genus *Podocarpus* and whose natural habitats are quite distinct, the presence of these compounds is not even diagnostic of the family. Moreover, no clear patterns of characteristic constituents emerge for the different genera or sub-sections of the family."

The second opinion on the question of the utility of chemistry in taxonomy of essential oil-bearing plants is expressed by Mirov, whose monograph (1961) on the *Pinus* turpentines

was earlier referred to. It will be recalled that his work covers the entire genus as it is at present known, and it is considered that the following quotations from his monograph are a fair summary of the present position; and although uttered specifically in reference to the *Pinus* turpentines, may equally well apply to other fields of phytochemistry:

"Some closely-related pines may possess turpentines of different compositions; on the other hand, it is known that two species taxonomically remote have turpentines of almost identical composition . . .

"The chemical composition of turpentine is not always correlated with the taxonomic position of a pine. One reason for absence of relationship is incomplete knowledge of chemical composition of pine turpentines. Another reason is that there is still a great deal of disagreement among botanists as to the classification of pines . . .

"Evolutionary development may also explain certain absences of relationship. Most likely, morphological and chemical characters have followed different paths of evolution.

"In correlating the composition of turpentine with the taxonomic position of a pine, one should remember that the genus *Pinus* of today is different from the genus of the Tertiary period. The oldest living species is probably not older than Miocene. The chemical relationship of pines that existed during the Jurassic was most likely different from what it is now. During the evolution of the genus, many ancient species became extinct, and many new species appeared. At present we have merely patches of an old biochemical pattern. Some of these patches are difficult to fit into the present structure of the genus; others fit very well and are useful in understanding the relationship of living pines . . .

"At present it would be futile to develop a natural classification of pines based on their chemical characters. We can merely claim now that chemistry and taxonomy of pine species often coincide, and that when morphological characters are ambiguous, a knowledge of chemistry of the turpentines may be useful."

From what has been said, the value of the chemistry of essential oils in relation to taxonomy appears limited. However, it is submitted that much more information is needed before assessing the worth of the systematic rôle of these substances. Indeed, the successes attending the application of other phytochemical products in this field should stimulate further research: a good

example is the weight of chemical evidence brought forward by Price (1963) and Ritchie (1964) to determine the taxonomic position of *Flindersia*.

Using modern methods, therefore, and having regard for some of the principles enunciated, the systematic examination of complete taxa of generic rank and higher should be undertaken. Some co-ordination between workers in different classes of plant product is required: this paper has been confined to volatile oils; that is, to compounds having boiling-points from, say, 150° C to 350° C. This is an arbitrary division of secondary plant products, and it is certain that the plant knows nothing of vapour pressures. The study of essential oils alone, therefore, does not present a complete biochemical picture. For example, Erdtman (1956), in studying heartwood extractives of *Pinus*, was able to distinguish not only the genus, but was also able to distinguish chemically the two sub-generic taxa, Haploxyton and Diploxyton. On the other hand, Mirov, working on the turpentine distilled from the oleo-resins, was unable to do this. The overall picture of the secondary chemical constituents of plants is needed, bearing in mind that some chemical compounds of different structure may be biochemically related, and that certain substances may arise through more than one biosynthetic pathway.

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