

PROCEEDINGS OF THE
FOURTH INTERNATIONAL CONGRESS
OF BIOCHEMISTRY

VIENNA 1958

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CONIFER CHEMISTRY AND TAXONOMY OF CONIFERS¹

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Our present views on the phylogenesis of plants are based essentially on botanical and plant geographical evidence. There is as yet no well-founded phylogenetic system, only a number of more or less "natural systems".

Evolution depends upon a combination of internal and external factors. "Mutation, recombination (of genic differences) and selection as well as isolation and extinction are responsible for groups and categories on all levels" (Stebbins).²

The internal factors are basically of a chemical nature and systematic chemical investigation should thus be able to contribute to the elucidation of phylogenetic problems.

"Chemical taxonomy" must, of course, be based on the occurrence of identical or related compounds in different series of plants and on knowledge of the biochemical systems involved in their formation. A prerequisite for chemical taxonomy is that the reference compounds should be produced by all specimens grown under comparable conditions.

Fortunately, as expected, this is usually the case, at least among the higher plants, although certain exceptions are known. External factors, such as the temperature, have some influence and should always be kept in mind. The proportions of the constituents, however, frequently vary within wide limits. When large chemical hereditary variations occur it is customary to speak about "chemical varieties". The chemist interested in taxonomic problems should pay attention more especially to the natural products which occur in phylogenetically old, comparatively unspecialized organs. Substances deposited in the "dead" parts of plants such as heartwood or bark are of special interest as they constitute definite end products, largely independent of seasonal variations and other external influences.

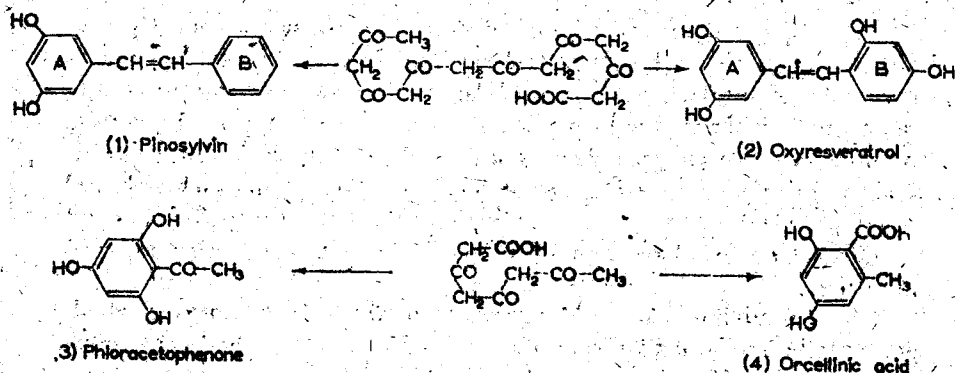
It is also advisable to take cognizance of the fact that organs which appear to be similar may biologically be of different origin, that is analogous instead of homologous, e.g. leaves and leaf-like organs formed from leaf

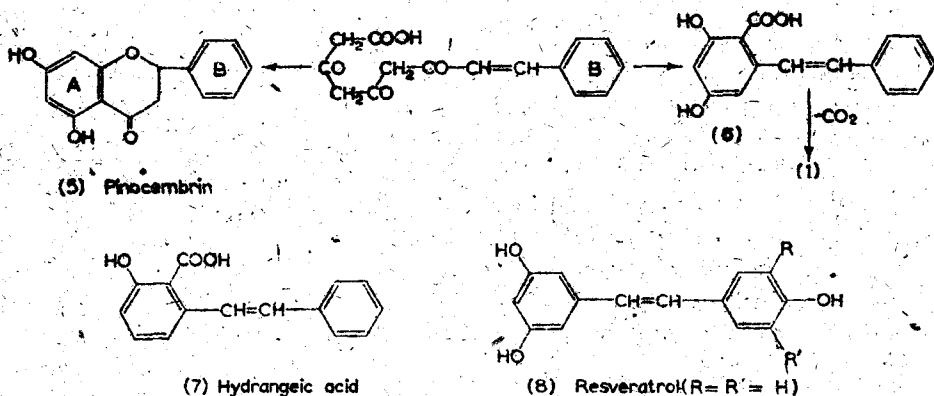
stalks. However, all chemical constituents possess some taxonomic interest even if only slight.

A phenomenon well known to all biologists is the "convergence" during evolution of plants of quite different origin; they may become so similar that it is tempting to assume a closer relationship than actually exists. In the same way identical or closely related compounds may occur in systematically quite unrelated groups of plants. A close phylogenetic relationship between plants or groups of plants should not be assumed simply because they have been found to contain identical or chemically related compounds. Many natural products have little taxonomic value because they occur in almost all plants (glucose, oleic acid, the common amino acids) or because they are produced exclusively by a single species. To be of greater taxonomic value, a compound, or preferably a certain pattern of compounds, should occur in larger groups of plants, e.g. a section, a subgenus, a genus or a family. It follows that it is difficult or impossible for a chemist to judge the systematic position of genera which embrace only a few species or are monotypic. Of course chemistry alone cannot give the final answer to taxonomic questions; it represents merely one method among many others and its importance should not be over-emphasized.

The presence of identical or closely related substances in plants of quite different systematic position may be due to the presence of similar biochemical systems but they may also have been formed along different biochemical pathways. It is therefore theoretically possible for identical substances to be "biosynthetically different" or biologically "analogous" instead of "homologous".

The stilbene derivatives pinosylvin (1) (Pinaceae) and oxyresveratrol (2) (Liliaceae) may be derived from acetic acid according to Collies' old hypothesis on the role of polyketetomethylenes in biosynthesis.² In the case of oxyresveratrol this is an especially attractive assumption since all four hydroxyl groups are at once correctly oriented:





However, on this hypothesis it is necessary to postulate a reduction of ring B in pinosylvin and it appears probable that this reduction would take place at a pre-aromatic stage since the biochemical feasibility of reductive elimination of phenolic hydroxyl groups does not seem to have been established.

Pinosylvin occurs in the heartwood of pines together with a series of flavonoids all possessing a non-hydroxylated B-ring and it is reasonable to assume that this is not merely a strange coincidence but that there is a close biosynthetic relationship between pinosylvin and the flavonoids.

The A-ring of the latter appears to be formed from "acetate" and the attached C_6C_3 -system via the shikimic-prephenic acid route.

The relationship between pinosylvin and for example pinocembrin (5) would then be analogous to that assumed on good grounds⁴ to exist between the members of the orcellinic acid (4) series and a large number of natural benzophenone derivatives of which phloracetophenone (3) (Rutaceae) is a particularly simple example.

According to this hypothesis pinosylvin would be formed by decarboxylation of a pinosylvin carboxylic acid (6) closely analogous to hydrangeic acid (7).

In view of this possibility we have searched for the carboxylic acid (6) or the corresponding isocoumarin (an analogue of hydrangenol) throughout our investigation on the pine genus but hitherto without positive result.

In this connexion it is of interest that chavicol methyl ether and cinnamic acid have been isolated from some pinewoods. The latter could be looked upon either as a secondary degradation product of pinosylvin or the associated flavonoids or as a stabilized or intercepted intermediate in their biosynthesis.

In addition to oxyresveratrol, *Veratrum grandiflorum* also contains another stilbene derivative, resveratrol (8) ($R = R' = H$), and the question arises whether this compound is formed simply from acetate or from

acetate and for example a *p*-cumaric acid unit. The tetra- and pentahydroxystilbenes (8) ($R = OH, R' = H$) and (8) ($R = R' = OH$) occurring in the heartwood of *Voucaperia macropetala*⁵ may be formed by hydroxylation of resveratrol, perhaps at an intermediate stage.

The confused biosynthetic relationships among the natural stilbenes have been further complicated by the discovery of 4-hydroxystilbene in the heartwood of *Pinus griffithii*.⁶ Pinosylvin and other typical pine heartwood components are also present. 4-Hydroxystilbene is the only natural stilbene derivative known that lacks hydroxyl groups in the "orcinol" position but at present it does not appear worth while speculating about its biosynthetic past.

This discussion shows how essential it is to elucidate the actual biosynthesis of a natural product in order to be able to assess its taxonomic value. In fact a knowledge of the biochemical systems involved in the biosynthesis of a natural product would certainly be of greater taxonomic value than the product itself. It is very probable that the biosynthesis of natural compounds will play a future role in chemical taxonomy comparable with that of embryology in classical taxonomy.

PINALES

The Genus Pinus

In our studies on the heartwood constituents of conifers we were anxious to begin with a systematic investigation of the extractives from the heartwood of pines because the genus *Pinus* is well defined and has a large number of species, about a hundred altogether. We have now investigated about half of them. Several specimens have been examined from many of these species and in one case, *Pinus silvestris*, several hundred of widely different geographical origin have been investigated. It is interesting to note that only one compound was found, and this only once, which could not be detected in other specimens of the same species. This shows that the pattern of heartwood constituents in pines is very constant.

We have, of course, examined wood from pines of both the subgenera *Diploxylon* and *Haploxylon* of the genus *Pinus* as well as from all sections and smaller groups recognized within these subgenera.

Pinosylvin (1), pinosylvin monomethyl ether and the flavanones (-)-pinocembrin (5) and (+)-pinobanksin (9) are found in almost all pines. These compounds form the main pattern of the phenolic constituents isolated from the subgenus *Diploxylon* (Table I).

The subgenus *Haploxylon* has a much more complex heartwood chemistry. The main feature is the occurrence of the stilbenes and flavanones with their respective hydrogenation and dehydrogenation products, the dibenzyls and the flavones. This may indicate that in the *Haploxylon*

TABLE I

Heartwood constituents of pines
(Classification according to Shaw)

HAPLOXYLON			Pinosylvin = P	P-monomethylether = PSM	Dihydro-P	Dihydro-PSM	Pinocembrin	Chrysin	Pinostrobin	Tectochrysin	Pinobanksin	Strobobanksin	Strobopinin	Cryptostrobin
Section	Sub-section	Species												
Cembra	Cembrae	1 <i>koraiensis</i> S. and Z.	+	+	+	+	+	+	+	+	+	+	+	+
		2 <i>cembra</i> L.	+	x	+	+	x	x	+	x	+	+	+	+
		3 <i>albicaulis</i> Eng.	+	x	+	x	+	+	+	+	+	+	+	+
	Flexiles	4 <i>flexilis</i> Jam.	?	+	+	+	+	+	+	+	+	+	+	+
	Strobi	5 <i>ayacahuite</i> Ehr.	+	+	+	+	?	+	?	+	+	+	+	+
		6 <i>lambertiana</i> Dougl.	+	+	+	+	+	+	x	x	+	x	x	?
		7 <i>parviflora</i> S. and Z.	+	+	+	+	+	+	+	+	+	+	+	+
		8 <i>formosana</i> Hay	+	+	?	+	+	+	+	+	+	+	+	+
		9 <i>peuce</i> Gris.	+	+	+	+	+	+	+	+	?	+	+	+
		10 <i>griffithii</i> M'Cl.	+	x	+	+	x	x	+	x	x	+	+	+
		11 <i>monticola</i> Dougl.	+	x	+	+	+	x	+	x	?	+	x	+
		12 <i>strobus</i> L.	+	x	+	+	+	x	x	x	x	x	x	x
Paracembra	Cembroides	13 <i>cembroides</i> Z.	+	+	+	+	+	+	+	?	?	+	+	+
	Gerardianae	14 <i>bungeana</i> Z.	+	+	+	+	+	+	+	+	+	+	+	?
		15 <i>gerardiana</i> Wall.	+	+	+	+	+	+	+	+	+	+	+	+
Balfourianae		16 <i>balfouriana</i> A. Murr	+	+	+	+	+	+	+	+	+	+	+	+
		17 <i>aristata</i> Eng.	?	x	+	x	x	+	x	+	+	+	+	+

(+ and - : presence or absence of compound as demonstrated by paper chromatography;
x : compound isolated.)

TABLE I (continued)

DIPLOXYLON			Pinosylvic = P	P-monomethylether = PSM	Dihydro-P	Dihydro-PSM	Pinoembrin	Chrysin	Pinoestrobin	Tecto-chrysin	Pinobanksin	Strobobanksin	Strobopinin	Cryptostrobin
Section	Sub-section	Species												
Parapinaster	Leio- phyllae	1 <i>leiophylla</i> S. and Ch. 2 <i>humholtzii</i> R. and F.	+	+	-	-	+	-	-	-	+	-	-	-
	Longi- foliae	3 <i>canariensis</i> Sm. 4 <i>longifolia</i> Rox	+	+	-	-	+	-	-	-	+	-	-	-
	Pi- neae	5 <i>pinex</i> L.	+	x	-	-	x	-	-	-	+	-	-	-
Pinaster	Laricines	6 <i>resinosa</i> Ait.	+	x	-	-	?	-	-	-	?	-	-	-
		7 <i>massoniana</i> Lamb	+	+	-	-	+	-	-	-	+	-	-	-
		8 <i>densiflora</i> S. and Z.	+	+	-	-	+	-	-	-	+	-	-	-
		9 <i>sylvestris</i> L.	x	x	-	-	+	-	-	-	+	-	-	-
		10 <i>mugo</i> Turr.	x	x	-	-	x	-	-	-	?	-	-	-
		11 <i>nigra</i> var. <i>poiretiana</i> Sch.	+	x	-	-	+	-	-	-	-	-	-	-
		12 <i>nigra</i> var. <i>aust.</i> (H.) Bad.	+	+	-	-	+	-	-	-	-	-	-	-
	Australes	13 <i>montezumae</i> Lamb	+	+	-	-	+	-	-	-	+	-	-	-
		14 <i>ponderosa</i> Doubl.	x	x	-	-	x	-	-	-	x	-	-	-
		15 <i>jeffreyi</i> Balf.	+	x	-	-	x	-	-	-	+	-	-	-
		16 <i>occidentalis</i> Sw.	+	+	-	-	+	-	-	-	+	-	-	-
		17 <i>palustris</i> Mill.	?	+	-	-	+	-	-	-	+	-	-	-
		18 <i>caribea</i> Mor.	-	+	-	-	+	-	-	-	+	-	-	-
		19 <i>taeda</i> L.	+	x	-	-	x	-	-	-	x	-	-	-
		20 <i>glabra</i> Walt.	+	+	-	-	+	-	-	-	+	-	-	-
		21 <i>echinata</i> Mill.	+	+	-	-	+	-	-	-	+	-	-	-

(+ and - : presence or absence of compound as demonstrated by paper chromatography;
x : compound isolated.)

TABLE I (continued)

DIPLOXYLON			Pinosylvin = P	P-monomethylether = PSM	Dihydro-P	Dihydro-PSM	Pinocembrin	Chrysin	Pinostrobin	Tecto-chrysin	Pinobanksin	Strobobanksin	Strobopinin	Cryptostrobin
Section	Sub-section	Species												
Pinaster	Insignes	22 <i>halepensis</i> Mill.	x	x	-	-	+	-	-	-	+	-	-	-
		23 <i>pinaster</i> Ait.	+	+	-	-	x	-	-	-	x	-	-	-
		24 <i>virginiana</i> Mill.	?	x	-	-	x	-	-	-	x	-	-	-
		25 <i>clausa</i> Vas.	+	+	-	-	x	-	(+)	-	x	-	-	-
		26 <i>rigida</i> Mill.	+	+	-	-	+	-	-	-	+	-	-	-
		27 <i>pungens</i> Lamb.	+	+	-	-	+	-	-	-	+	-	-	-
		28 <i>banksiana</i> Lamb.	x	x	-	-	x	-	-	-	x	-	-	-
		29 <i>contorta</i> var. <i>latif.</i> Eng.	x	x	-	-	x	-	-	-	x	-	-	-
		30 <i>muricata</i> D. D.	+	+	-	-	+	-	-	-	+	-	-	-
		31 <i>attenuata</i> Lemm.	?	+	-	-	+	-	-	-	+	-	-	-
		32 <i>radiata</i> D. D.	-	x	-	-	x	-	-	-	x	-	-	-
		33 <i>radiata</i> var. <i>insign.</i> Dougl.	+	+	-	-	+	-	-	-	+	-	-	-
	Macrocarpae	34 <i>sabiana</i> Dougl.	+	+	-	-	+	-	-	-	+	-	-	-
		35 <i>coulteri</i> D. D.	+	+	-	-	+	-	-	-	+	-	-	-

(+ and - : presence or absence of compound as demonstrated by paper chromatography; x : compound isolated.)

pinus there is available an oxidation-reduction system capable of transferring hydrogen from the flavanones to the stilbenes. Most probably, the genetic changes responsible for these characteristic differences are intimately related to those that once caused the separation of the subgenera *Diploxylon* and *Haploxylon*. It is possible that these chemical differences are due to a loss mutation, in which case the *Haploxylon* pines would be forerunners of the *Diploxylon* pines. Both subgenera are known from the early cretaceous period and it is, of course, possible that the separation started or took place even at a pre-*Pinus* stage. Another very obvious difference between the *Diploxylon* and *Haploxylon* pines is that the latter appear to possess more powerful methylating systems. Almost all *Haploxylon* species contain (-)-pinocembrin (5), its 7-methyl ether, (-)-pino-

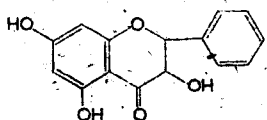
strobilin (10), and their dehydrogenation products chrysin (11) and tectochrysin (12). Two subsections of the *Haploxydon* pines also contain carbon methylated flavanones and flavones such as strobopinin (13),^{7,8} cryptostrobin (14),^{7,8} strobobanksin (15) and strobochrysin (16).

That these compounds are formed by carbon methylation and not by incorporation of propionic acid is very probable in view of the many examples known of progressive carbon methylation of resorcinol and phloroglucinol derivatives e.g. butanofilicinic acid and leptospermone and we have recently encountered another very interesting example of the same type.⁹

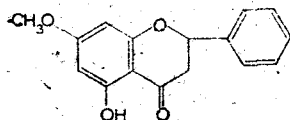
"Ceroptene", found in the fern *Pityrogramma triangularis*, has been shown to possess structure (17) (or the tautomeric structure) and desmethoxy-matteucinol from the fern *Matteucia orientalis* was long ago found to be (18).

In the former case we have carbon methylation twice in one position and in the latter once in two positions. "Ceroptene" can be regarded as a very interesting "missing link" between the flavones and the fern constituents of the filicinic acid group.

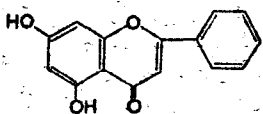
The bark and the heartwood of pines sometimes contain different flavonoids. Aromadendrin (19), taxifolin (20), quercetin (21), dihydromyricetin (22), myricetin (23) and pinobanksin (9) have been isolated from the bark of *P. contorta*,¹⁰ from *P. ponderosa* (like *P. contorta* also of the *Diploxydon* group); quercetin, taxifolin, pinoquercetin (6-methylquercetin) and pinomyricetin (6-methylmyricetin).¹¹



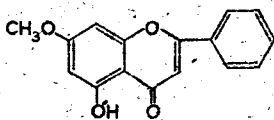
(9) Pinobanksin



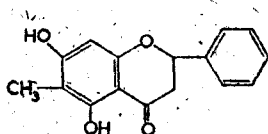
(10) Pinostrobin



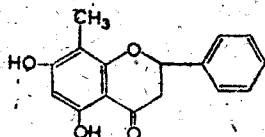
(11) Chrysin



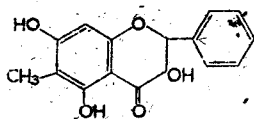
(12) Tectochrysin



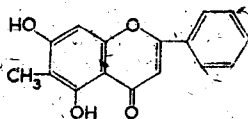
(13) Strobopinin



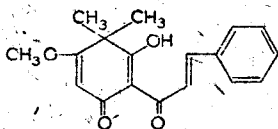
(14) Cryptostrobin



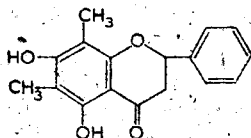
(15) Strobobanksin



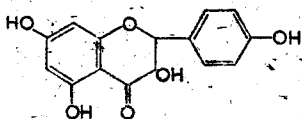
(16) Strobachrysin



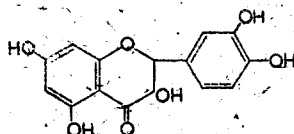
(17) "Ceroptene"



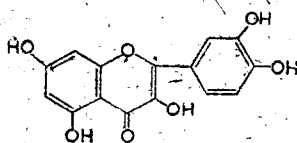
(18) Desmethoxymatteucinol



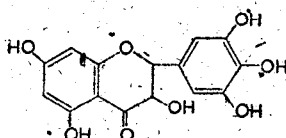
(19) Anomadendrin



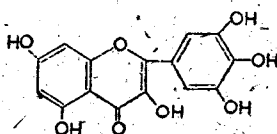
(20) Taxifolin



(21) Quercetin



(22) Dihydromyricetin



(23) Myricetin

This may appear strange at first sight but must certainly be due to the formation of bark and wood from different cambia. This observation is an indication that at least some of the heartwood compounds are formed in the cambium from precursors synthesized elsewhere, e.g. in the leaves, and then transported to the dead or dying inner part of the sapwood. It was therefore not unexpected to find small amounts of the heartwood constituents also present in the sapwood.

The stilbene-flavone pattern is very characteristic of the pine genus; the variations in the pattern indicate a possibility of subdividing the genus by

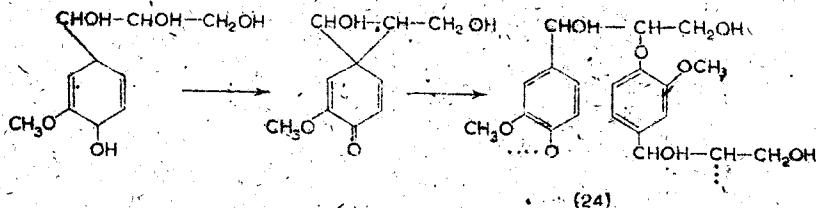
purely chemical means into smaller groups and it is interesting to find that these coincide closely with those already recognized by botanists.

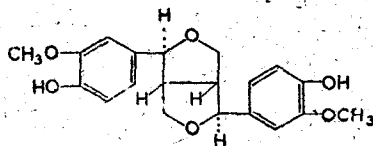
Cyclitols, especially pinitol, occur in the leaves of practically all conifers and pinitol is present in the heartwood of several *Haploxyton* pines, sometimes in large quantities. They are not yet of any great taxonomic importance. The same applies to the lower terpenes from leaves and from wood oleoresins. The latter have been studied extensively by Mirov¹² but there appears to be no clear-cut difference between the terpenes in *Diploxyton* and *Haploxyton*. Pinene, borneol, limonene, and many other terpenes occur scattered throughout the conifers. Some higher terpenes appear to have a more restricted distribution and are taxonomically more interesting. Diterpenes of the abietic and dextropimaric acid types probably occur in all pines but they have not yet been studied from a systematic point of view.

The resins exuded from wounds after the cessation of the primary oleoresin flow are of a special type. As well as abietic acid and a number of simple phenylpropane derivatives (caffeic acid, ferulic acid, *p*-cumaric acid) these wound resins contain lignans, e.g. (+)-pinoresinol (25) thought to have been formed from simple phenylpropane derivatives, e.g. coniferyl alcohol or some biological equivalent by enzymatic dehydrogenation. (±)-pinoresinol is formed *in vitro* by dehydrogenation of coniferyl alcohol as has recently been shown by Freudenberg¹³.

The lignins are very probably formed from similar precursors and following an early suggestion by the writer¹⁴ it has generally been assumed that they are produced by dehydrogenation of such compounds, conifer lignins being formed mainly from coniferyl alcohol. Only a few conifer lignins contain any large proportions of syringyl elements (*Tetraclinis* and a few podocarps). It should be noted, however, that coniferin and syringin, unlike caffeic acid, ferulic acid etc., appear to be rare and have been demonstrated in only a few plants.¹⁵ It is still not certain that coniferyl alcohol is the immediate precursor of conifer lignin.

Long ago the author pointed out that the dehydration of suitably substituted phenylpropanes would be equivalent to dehydrogenation and the structural element (24) which has attracted considerable attention at the present time in relation to hypothetical lignin structures could arise by the following, or similar (enzymatic!) series of reactions:





(25) Pinoresinol

This possibility is even more attractive in the light of recent work by Wiastein and Baird¹⁶ on the reaction of *p*-hydroxy- β -bromoethyl benzene and of similar studies by Dreiding¹⁷ and is also worth consideration in connexion with several other biogenetic problems, for instance the relationship between flavones and isoflavones, the formation of the bis-flavones etc.

There is, however, still much to be said in favour of the dehydrogenation hypothesis, e.g. the occurrence of diphenyl linkages in lignin.^{18,19}

Lignin has no great taxonomic value except in the delimitation of large taxonomic categories such as gymnosperms and angiosperms.

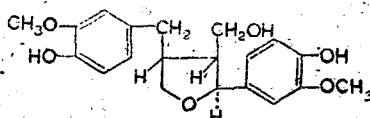
This also seems to be the case with the components of the outer wax-layer of the leaves of non-deciduous conifers which contains a mixture of long chain hydrocarbons, alcohols and polyestolides of sabinic acid (ω -hydroxy lauric acid) and juniperic acid (ω -hydroxy palmitic acid).²⁰

OTHER GENERA OF THE ORDER PINALES

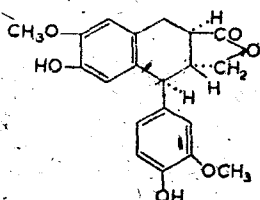
Like *Pinus*, the genus *Pseudotsuga* is found only in the northern hemisphere and is restricted to western North America and eastern Asia. Botanically as well as chemically it appears to be rather closely related to the pines. Both heartwood and bark of *Pseudotsuga douglasii* contain large amounts of taxifolin contaminated by small amounts of aromadendrin, pinobanksin and pinocembrin.²¹ Pinosylvin is absent. The wound-resin is similar to that of the pines and contains abietic acid, type resin acids, but no large amounts of pinoresinol and similar lignans which could be precipitated as salts from alcoholic solutions by potassium hydroxide.²²

The larches, *Larix*, contain taxifolin, aromadendrin and the lignan lariciresinol (26) which is closely related to pinoresinol. Quite recently it has been reported that the resin acids of *Larix kaempferi* are of the common *Pinus-Picea*-type.²³ The wood of many spruce (*Picea*) species contains the lignan conidendrin (27). According to recent investigations the wood of Norway spruce (*Picea excelsa*) contains small amounts of a whole series of lignans including pinoresinol, matairesinol (28) and hydroxymatairesinols.²⁴ The wound resin is the most convenient source of pinoresinol. No flavones have been found.

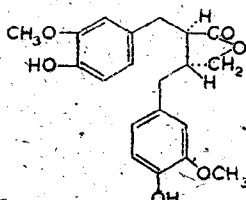
The hemlocks (*Tsuga*) appear to be less resinous than the above genera but like *Picea* they contain conidendrin.



(26) Loriciresinol



(27) Conidendrin



(28) Matairesinol

The true cedars, *Cedrus*, appear to be divergent. The woods of this small genus contain an interesting group of sesquiterpenes, of which the best known are the atlantones. It would be of a considerable interest to investigate the nonvolatile extractives from these trees to see whether they contain any characteristic constituents known from other Pinaceae, e.g. flavones.

Unfortunately very little is known about the constituents of the systematically interesting firs, *Abies*, though several appear to contain resin acids and *Keteleeria* and *Pseudolarix* remain chemically almost untouched.

The northern hemisphere order Pinales (family Pinaceae) has been carefully studied botanically and subdivided into a series of characteristic genera; it is therefore not surprising that the chemical results on the whole are in good agreement with the botanical classification. This is also an indication of the usefulness of chemical studies from a taxonomic point of view.

PODOCARPALES AND ARAUCARIALES

The Podocarpaceae (family: Podocarpaceae) and Araucariaceae (family: Araucariaceae) are essentially southern hemisphere orders. They have been less intensely studied by botanists and the various genera are, taxonomically, not so well defined. It would therefore not be unexpected if these groups showed some conflict between chemical and botanical results. Unfortunately the chemistry of these orders has been very incompletely studied and it is therefore uncertain whether the few known heartwood constituents are really representative of the genera and subgenera into which the families have been divided.

Botanically the large genus *Podocarpus* and the related somewhat smaller genus *Dacrydium* are heterogeneous and there is chemical evidence for this

as is shown by a perusal of Table II showing the known heartwood constituents of a series of species belonging to these genera.

TABLE II

Constituents of some Podocarpus and Dacrydium species

Genera and species	Sections	Phyllocladene	(29)	Rimuene	(30)	Ferruginol	(31)	9-Ketoferruginol	(32)	Totarol	(33)	Hydroxytotarol	Podocarpic acid	(34)	Conidendrin	(27)	Matairesinol	(28)	Manool	(35)	Manoyloxide	(36)	Ketomanoyloxide	(37)
<i>Podocarpus totara</i>	<i>Eupodocarpus</i>			+						+		+												
<i>totara</i> var. <i>hallii</i>	<i>Eupodocarpus</i>		+																					
<i>macrophylla</i>	<i>Eupodocarpus</i>		+																					
<i>ferrugineus</i>	<i>Stachycarpus</i>		+			+																		
<i>spicatus</i>	<i>Stachycarpus</i>		+													+		+						
<i>dacrydioides</i>	<i>Dacrycarpus</i>												+	+										
<i>cupressinum</i>	<i>Dacrycarpus</i>												+	+										
<i>Dacrydium cupressinum</i>				+		+		+		+		+	+	+										
<i>colensoi</i>			+																			+	+	
<i>biforme</i>			+																	+				
<i>bidevillii</i>																				+				
<i>kirkii</i>			+																					

Brandt and Thomas concluded that *Dacrydium cupressinum* rightly belongs to the podocarps with which it has several compounds in common and it will probably be placed in one of the genera into which the podocarps will be subdivided in a future revision of the genus.

The taxonomic position of *Dacrydium franklinii* (eugenol methyl ether) also appears worth reconsidering. *Dacrydium elatum* has been stated to contain cedrol but this is obviously erroneous.

The genera *Araucaria* and *Agathis* (Araucariaceae) are little known from a chemical point of view and investigation has been mainly confined to the resinous exudates. It is interesting that *Araucaria angustifolia* contains pinoresinol (25) and its dimethyl ether.²⁶ *Araucaria bidevillii* produces a resin from which a small amount of agathene dicarboxylic acid (38) has been