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REVIEW ARTICLE

SOME ASPECTS OF THE CHEMISTRY OF THE ORDER PINALES*

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Abstract—A brief review of the chemistry of the conifer order Pinales is given. Some chemical relationships of taxonomic interest are pointed out. Unpublished results on the bark extractives of *Pinus sylvestris* and *Picea abies* and on the constituents of the oleoresin of the latter species and *Larix decidua* are briefly reported.

INTRODUCTION

THE CONIFERS include some 650 species of woody plants whose origin dates back at least two hundred million years (late Paleozoic). Some authors divide this taxon into four orders, Pinales, Cupressales, Podocarpales and Araucariales, whilst others regard these orders to have only the rank of families. Frequently included are Taxales (*Taxus* and *Torreya*) and Cephalotaxales (*Cephalotaxus* and *Amentotaxus*) but these orders are often regarded as representing separate lines of evolution.

TABLE 1. THE ORDER PINALES (FAMILY PINACEAE)

Genus	No. of species	Genus	No. of species
Abies	52	*Picea*	40
Cathaya	2	*Pinus*	94
Cedrus	4	*Pseudolarix*	1
Keteleeria	6	*Pseudotsuga*	7
Larix	9	*Tsuga*	10

The order Pinales (Table 1) has only one family, Pinaceae, divided into several genera: *Abies, Cathaya, Cedrus, Keteleeria, Larix, Picea, Pinus, Pseudolarix, Pseudotsuga* and *Tsuga.* Some of these genera are large, e.g. *Abies, Picea* and *Pinus* and, indeed the genus *Pinus* is one of the largest of the conifers.†

The almost exclusively northern hemispheric order Pinales includes many commercially important forest trees and some of them have been fairly well investigated from a chemical point of view. In this review the intention is to present some aspects of the chemistry of the wood extractives of Pinales species. The extractives of bark and other tissues of some species will also be considered.

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* Based on a paper read at the Wood Extractives Symposium, 161st Meeting of the American Chemical Society in Los Angeles in April 1971.

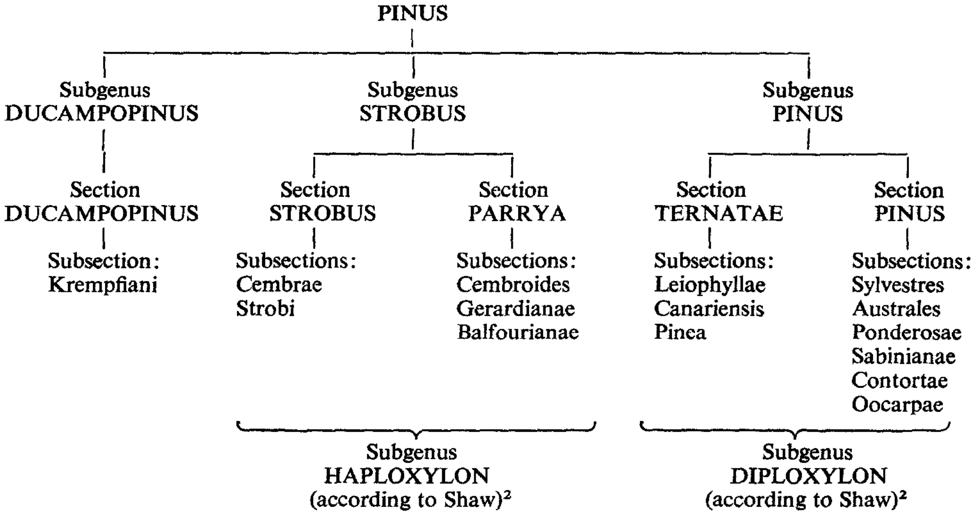
† Unless otherwise stated the names of species and higher taxa are those given in *A Handbook of Coniferae and Ginkgoaceae* (by W. DALLIMORE and A. B. JACKSON) (4th edn revised by S. G. HARRISON), Edward Arnold, London (1966).

THE GENUS *PINUS*

The genus *Pinus*, the true pines, has been carefully studied by several taxonomists and is a well-defined genus. Therefore, it is also suited for systematic chemotaxonomic investigations. Pioneering studies of this kind have been carried out by Erdtman.[1]

Pine heartwoods contain a variety of compounds formed along various biosynthetic pathways: carbohydrates, cyclitols, phenols, fatty acids and terpenoids. Taken together, these substances provide a pattern of chemical characters by means of which one can differentiate between pines and all other plants. Clearly, the chemical characters of other tissues, such as bark, needles, pollen, etc. should be included in a full chemical description of the species.

TABLE 2. CLASSIFICATION OF THE GENUS *Pinus* ACCORDING TO CRITCHFIELD AND LITTLE[4]



The genus *Pinus* has been divided into two subgenera, Haploxylon and Diploxylon, according to Shaw.[2] The classification of pines has since then been updated by many authors (see ref.[3]). More recently, Critchfield and Little[4] have divided the genus into three subgenera, Ducampopinus, Strobus and Pinus. The genus has been further divided into 5 sections, 15 subsections and 94 species (Table 2).

The phenolic heartwood constituents of about 80 pine species have been investigated. Most of this work was carried out about 20 yr ago[5] but we have recently repeated[6] part of it using improved techniques and have extended the investigation to include some species which had not been studied previously.

Pinosylvin, its monomethyl ether and the flavones (—)-pinocembrin and (+)-pinobanksin are found in almost all pines (Fig. 1). These compounds form the main pattern of

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[1] H. ERDTMAN, *Chemotaxonomy and Serotaxonomy* (edited by J. G. HAWKES), p. 235, Academic Press, London (1968); and references cited therein.

[2] G. L. SHAW, *The Genus Pinus*, Arnold arboretum No. 5, Cambridge, Mass. (1914).

[3] N. T. MIROV, *The Genus Pinus*, p. 483, The Ronald Press, New York (1967).

[4] W. B. CRITCHFIELD and E. L. LITTLE, JR., U.S. Department of Agriculture, Washington, D.C., Forest Service, Miscellaneous Publ. 991 (1966).

[5] G. LINDSTEDT, *Acta Chem. Scand.* **5**, 129 (1951).

[6] H. ERDTMAN, B. KIMLAND and T. NORIN, *Bot. Mag. Tokyo* **79**, 499 (1966).

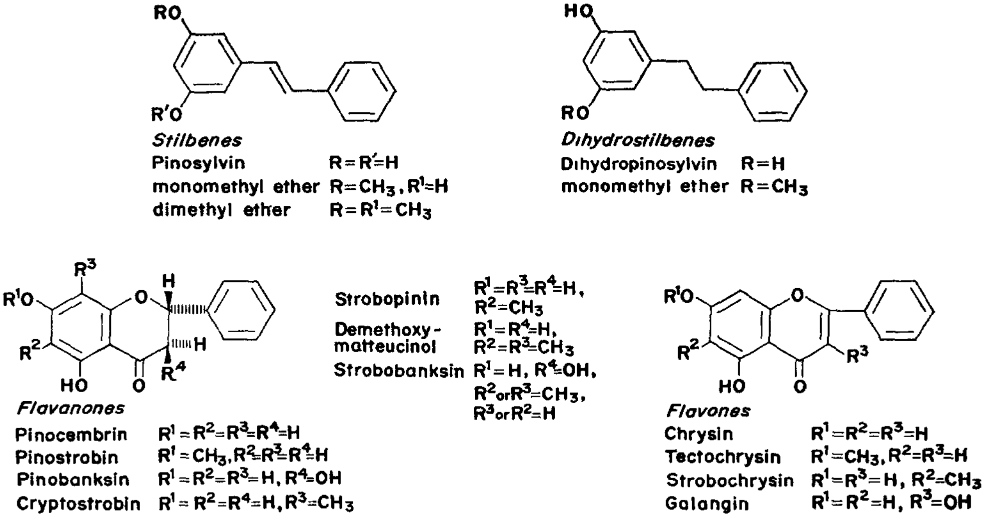

FIG. 1. PHENOLIC WOOD CONSTITUENTS OF *Pinus* SPECIES.

the phenolic constituents isolated from the subgenus Pinus (Diploxylon according to Shaw[2]). In most cases only a single or a few wood samples of each species were investigated but the consistence of the pattern appears to guarantee that it is typical of Diploxylon.

The subgenus Strobus (Haploxylon according to Shaw[2]) has a much more complex heartwood chemistry. The main feature is the occurrence of the stilbenes together with their hydrogenation products, the dibenzyls, and of the flavanones and their dehydrogenation products, the flavones. There are also some interesting *C*-methylated flavanoids, e.g. strobopinin and cryptostrobin which occur in species belonging to section Strobus (subsection Strobi) and those of section Paraya (subsection Gerardianae).

Erdtman[7] has suggested that the genetic changes responsible for these characteristic differences may be related to those that once led to the separation of the subgenera Diploxylon and Haploxylon. It is possible that these chemical differences are due to a loss resulting from a mutation in which case the Haploxylon pines could be regarded as being more primitive than the Diploxylon pines. Both subgenera are known from the early Cretaceous period and it is possible that the separation took place even at a pre-*Pinus* stage.

A few years ago we investigated[8] a pine, *P. krempfii* Lecompte, which differs to such an extent from other pines that some botanists regard it as belonging to a monotypic genus, *Ducampopinus krempfii* (Lecompte) Chevalier or at least to a subgenus of its own. Some authors have apparently even considered it to be a hybrid of a pine and a *Keteleeria* or *Pseudolarix* species. *P. krempfii* grows in the Nhatrang region of Vietnam. It has a smooth bark and fairly broad leaves (up to 5 mm) in pairs. Since there is only a single vascular bundle in the leaves, Florin[9] considered it simply to be an unusual Haploxylon pine. The heartwood chemistry of *Pinus krempfii* differs distinctly from that of Diploxylon pines but

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[7] H. ERDTMAN, *Fourth International Congress of Biochemistry. Biochemistry of Wood* (edited by K. KRATZL and G. BILLEK), Vol. II, Pergamon Press, Oxford (1959).

[8] H. ERDTMAN, B. KIMLAND and T. NORIN, *Phytochem.* 5, 927 (1966).

[9] R. FLORIN, *Kgl. Svenska Vetenskapsakad. Handl. Tredje ser.*, 10, 339 (1931).

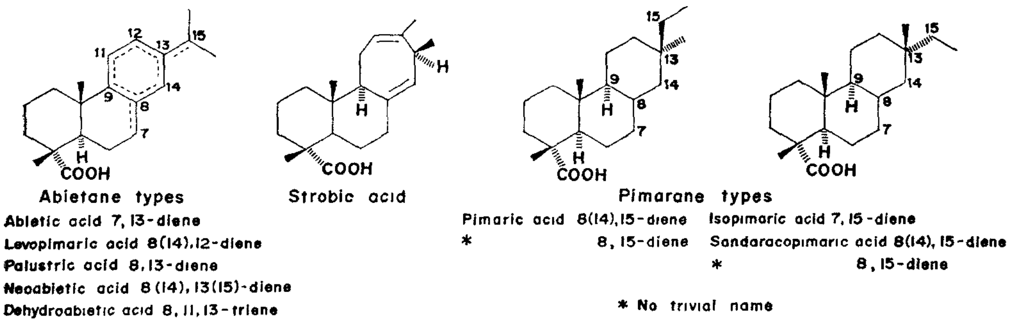

FIG. 2. RESIN ACIDS OF PINALES SPECIES.

there are all the characteristics of the Haploxylon pattern. From a chemical point of view it seems to agree particularly well with the members of the subsection Gerardianae.

Resin acids of the abietane and pimarane types (Fig. 2) and related compounds such as the corresponding aldehydes or alcohols are very characteristic constituents of the oleoresin of pine wood. Other characteristic constituents are monoterpenoids, particularly α- and β-pinene, which occur in most of the pines so far studied. However, some pines produce β-phellandrene, e.g. *P. contorta*. Crosses between this pine and the α-pinene producing *P. banksiana* result in plants producing mixtures of these terpenes.[3,10]

According to Shaw[2] *P. jeffreyi* is to be regarded as a variety of *P. ponderosa*. This species produces an unusual turpentine which consists mainly of *n*-heptane.[3,10] This hydrocarbon is evidently in no way directly related to the terpenes. Mirov[3,10] considered *P. jeffreyi* a separate species which should be transferred to the subsection Sabinae (Macrocarpae according to Shaw),[2] to which another notable heptane producer, *P. sabiniana*, belongs. *P. jeffreyi* hybridizes with *P. ponderosa* and the offspring contains constituents from both parent species.

Pines belonging to Shaw's Macrocarpae and also many Haploxylon pines contain mixtures of heptane, undecane and various terpenes.[3] It is possible that most pine turpentines contain at least traces of paraffin hydrocarbons.

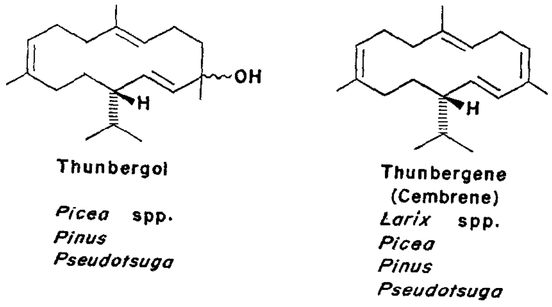

FIG. 3. MACROCYCLIC DITERPENOIDS OF PINALES SPECIES.

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[10] N. T. MIROV, *Composition of Gum Terpentines of Pines*, U.S. Dept. Agric. Forest Service, *Techn. Bull. No. 1239* (1961).

A number of sesquiterpenes and higher terpenes have been isolated from pines but have not been studied from a systematic point of view. Some of them appear to have a restricted distribution and are therefore of special taxonomic interest.

Thunbergene is an unusual macrocyclic diterpene hydrocarbon (Fig. 3) which was isolated from *P. thunbergii* by a Japanese group.[11,12] The hydrocarbon was originally named thumbelene[11,13] but this was later[12] correctly changed to thunbergene. It was found to be identical with the 'cembrene' of *P. albicaulis* isolated by Mirov.[14,15] The structure of thunbergene (cembrene) was determined independently by Akiyoshi[12] and Dauben[16] and their co-workers. Thunbergene and related compounds may be restricted to some groups of pines. It has not as yet been detected in *P. sylvestris.*

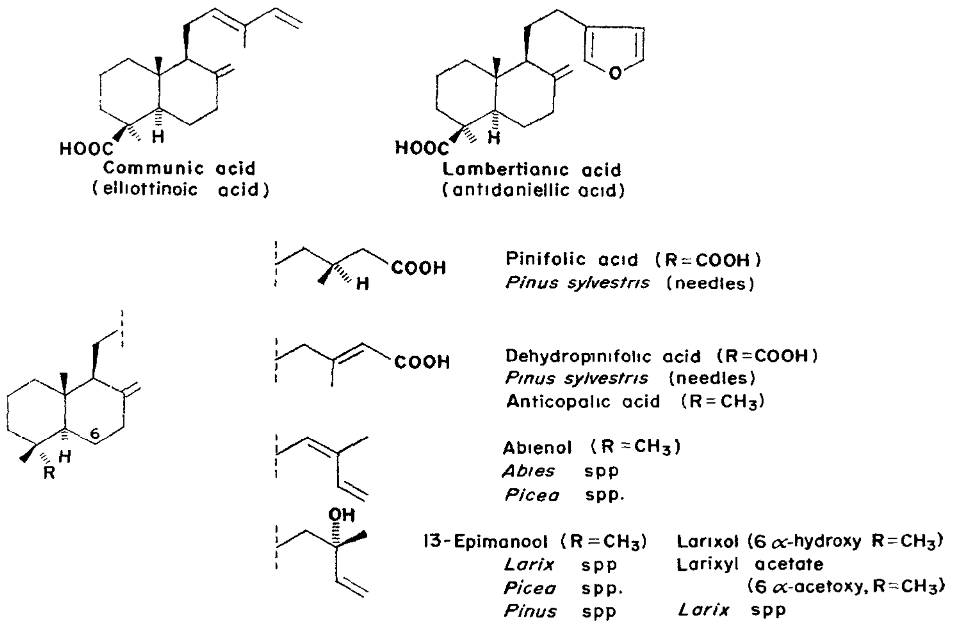

FIG. 4. DITERPENOIDS OF LABDANE TYPE IN PINALES SPECIES.

Some labdane diterpenoids have been isolated from pines. Lambertianic (antidaniellic) acid and communic (elliottinoic) acid (Fig. 4) belong to this class and occur together with the common resin acids in *P. lambertiana*[17] (also in *P. cembra* var. *sibirica*[18]) and *P. elliottii*[19] respectively. These acids have axial carboxyl groups in contrast to the equatorial carboxyl

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[11] S. AKIYOSHI, *Repts. Imp. Ind. Research Inst., Osaka Japan* **17**, No. 10, p. 1 (1937); *Chem. Abs.* **31**, 8172 (1937).

[12] H. KOBAYASHI and S. AKIYOSHI, *Bull. Chem. Soc. Japan* **35**, 1044 (1962).

[13] Y. SEBE, *J. Chem. Soc. Japan* **56**, 1118, 1137 (1935).

[14] A. J. HAAGEN-SMITH, T.-H. WANG and N. T. MIROV, *J. Am. Pharm. Assn. Sci. Ed.*, **40**, 557 (1951).

[15] Ref. 3, p. 497.

[16] W. G. DAUBEN, W. E. THIESSEN and P. R. RESNICK, *J. Am. Chem. Soc.* **84**, 2015 (1962).

[17] W. G. DAUBEN and V. F. GERMAN, *Tetrahedron* **22**, 679 (1966).

[18] N. K. KASHTANOVA, A. I. LISINA, A. K. DZIZENKO and V. A. PENTEGOVA, *Izv. Sib. Otd., Akad. Nauk SSSR, Ser. Khim. Nauk*, p. 126 (1967); *Chem. Abs.* **67**, 64571 (1967).

[19] N. M. JOYE, JR., E. M. ROBERTS, R. V. LAWRENCE, L. J. GOUGH, M. D. SOFFER and O. KORMAN, *J. Org. Chem.* **30**, 429 (1965).

groups of the common resin acids. In the needles of *P. sylvestris* two diterpene acids of labdane type, pinifolic and dehydropinifolic acid (Fig. 4), have been isolated.[20] These two acids on the other hand, have normal carboxyl group configuration of the resin acids. It is interesting to note that these two acids occur only in the needles and have not been detected in other parts of the tree (bark, cambium region, sapwood, heartwood or root).

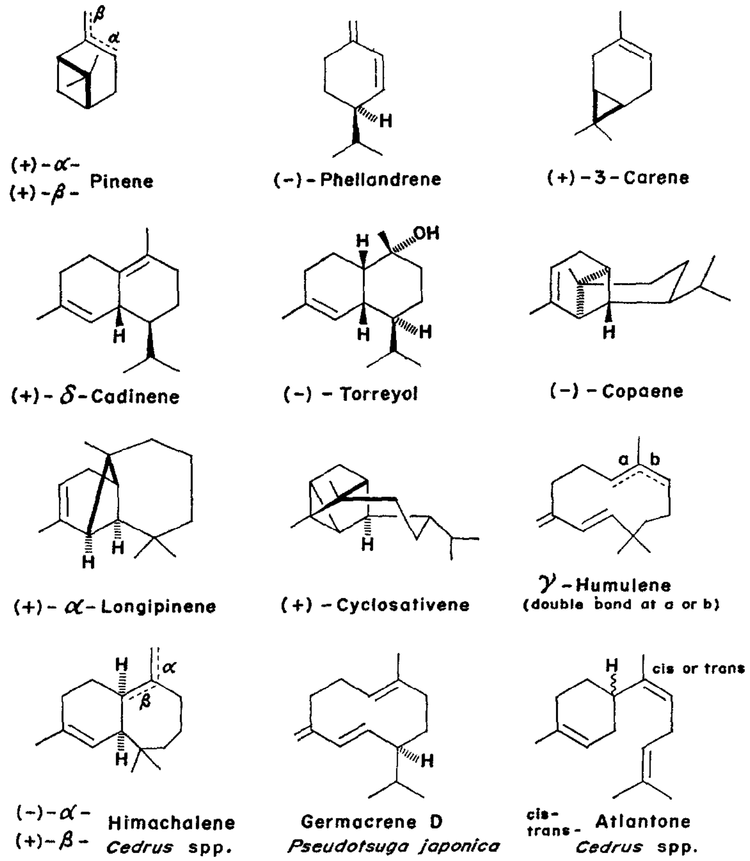

FIG. 5. SOME MONO- AND SESQUITERPENES OF PINALES SPECIES.

Recently, a new labdane diterpene, anticopalic acid (Fig. 4), has been isolated from the bark and wood extracts of western white pine, *P. monticola*.[21] In contrast to the previously mentioned acids this compound possesses a gem-dimethyl group at C(4).

The turpentine fractions of *P. sylvestris* and *P. albicaulis* have recently been studied in detail by Westfelt.[22] Using advanced isolation and identification techniques he isolated and characterized a number of sesqui- and diterpenes of which some were new, or isolated for the first time from Pinaceae. It is interesting to note that the (+)-δ-cadinene and the (−)-torreyol (Fig. 5) present in these two pine species are of the opposite absolute configurations

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[20] T. NORIN, S. SUNDIN and O. THEANDER, *Acta Chem. Scand.* **25**, 607 (1971).

[21] D. F. ZINKEL, J. K. TODA and J. W. ROWE, *Phytochem.* **10**, 1161 (1971).

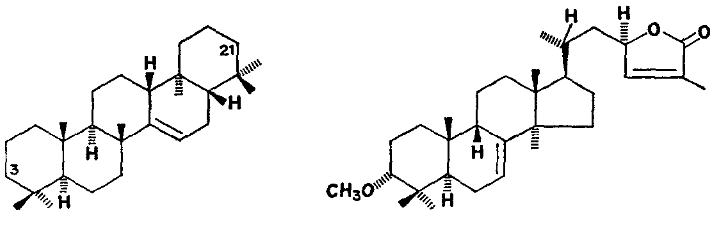
[22] L. WESTFELT, *Svensk Kemisk Tidskr.* **79**, 825 (1967).

with respect to those found in *P. sibirica*.[23] Westfelt[22] has suggested that this difference may be due to the presence of antipodal enzymes in *P. sibirica* or that there are two different types of cyclization mechanism operating in the biosyntheses of these compounds. This would also explain the co-occurrence of copaene and α-longipinene in *P. sylvestris*, since these two sesquiterpenes possess apparent opposite absolute configurations.

TABLE 3. SERRATANE TRITERPENES IN PINALES BARK

	Pinus	*Picea*
3α,21α-Dimethoxy-14-serratene	x	
3β,21α-Dimethoxy-14-serratene	x	
3β,21β-Dimethoxy-14-serratene	x	
3α-Methoxy-14-serraten-21β-ol	x	x
3β-Methoxy-14-serraten-21α-ol	x	x
3β-Methoxy-14-serraten-21β-ol	x	x
3α-Methoxy-14-serraten-21-one	x	x
3β-Methoxy-14-serraten-21-one	x	x
21β-Methoxy-14-serraten-3β-ol	x	
21α-Methoxy-14-serraten-3-one		x
21β-Methoxy-14-serraten-3-one	x	x
14-Serratene-3β,21α-diol (serratenediol)	x	x
14-Serratene-3α,21β-diol	x	
14-Serratene-3β,21β-diol	x	x
14-Serraten-16-on-3β,21β-ol	x	
14-Serraten-21-on-3α-ol	x	
14-Serraten-21-on-3β-ol	x	x

It is of considerable interest to note that the pine resins exuded from wounds after the cessation of the primary oleoresin flow appear to differ in composition from the primary oleoresin. The latter is rich in terpenoids, whereas the exuded resin contains considerable amounts of simple phenylpropane derivatives, e.g. caffeic acid, ferulic acid, *p*-coumaric acid and lignans, such as (+)-pinoresinol, containing 'coniferyl' elements characteristic for conifer lignins.



14 - Serratene derivatives
(cf Table 3)

Abieslactone

Abies mariesii	(bark, needles)
A. amabilis	(bark)
A. procera	(bark)

FIG. 6. TRITERPENOIDS FROM PINALES BARK.

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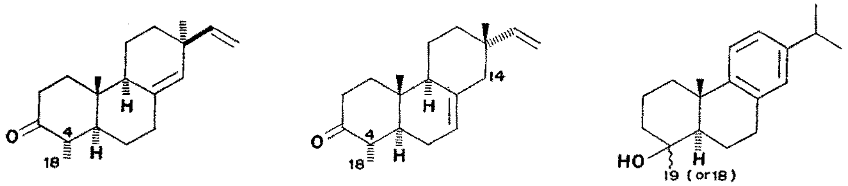
[23] V. A. PENTEGOVA, O. MOTL and V. HEROUT, *Collection Czech. Chem. Commun.* **26**, 1362, 1372 (1961).



19-Norpimara-8(14),15-dien-3-one (also 18-norpimara-8(14),15-dien-4-ol)

19-Norisopimara-7, 15-dien-3-one (also 19-norisopimara-8(14),15-dien-3-one, 18-norisopimara-7, 15-dien-4-ol 18-norisopimara-8(14),15-dien-4-ol)

18-Nordehydroabietan-4-ol 19-Nordehydroabietan-4-ol

FIG. 7. NORDITERPENOIDS FROM THE BARK OF *Pinus* SPECIES.

The bark extractives of some pines have been investigated.[24–28] Many of the bark constituents differ from those of the wood. Apart from the characteristic wood oleoresin constituents, the bark contains a number of compounds which appear to be tissue-specific, e.g. triterpenes of the serratene type (Fig. 6 and Table 3),[25–29] norditerpenoids (Fig. 7),[27] and a number of phenolic constituents.

Some low molecular weight extractives of the needles and of other tissues of a few pine species have been investigated. Considerable variations in composition of the extractives of the needles including, in some cases, seasonal variations have thus been reported.[30] However, very much remains to be done to provide us with a more systematic knowledge of the very interesting and highly complex phytochemistry of the pines.

THE GENUS *PICEA*

Although this genus is large and includes a number of forest trees of commercial importance, it has not been studied chemically in such detail as the pines. For example, the wood extractives of only a few species have so far been investigated. Resin acids of the abietane and pimarane types together with lignans appear to be characteristic constituents of these trees.

Owing to the commercial significance of *Picea abies*, Common Spruce, and because wood extracts of this species are readily obtainable in quantity, the wood extractives have been studied by a large number of investigators. Detailed information concerning the extractive contents of this wood and the composition of the extracts is available and has recently been reviewed.[31]

It is interesting to note that significant differences exist between the composition of the oleoresin from the resin canals and the composition of the wood extractives.[31] The oleoresin from the resin canals constitutes about 45% of the total non-volatile extractives in the wood and it contains negligible amounts of fatty acids, glycerides, waxes and sterols. Since these compounds are important wood constituents, they should be localized mainly to the parenchymatous wood rays. Resin acids and other terpenoids should be characteristic resin

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[24] J. W. ROWE and J. H. SCROGGINS, *J. Org. Chem.* **29**, 1554 (1964).
[25] J. W. ROWE and C. L. BOWER, *Tetrahedron Letters* 2745 (1965).
[26] J. W. ROWE and C. L. BOWER, *Phytochem.* **6**, 151 (1967).
[27] T. NORIN and B. WINELL, *Acta Chem. Scand.* **25**, 611 (1971).
[28] T. NORIN and B. WINELL *Acta. Chem. Scand.* in press.
[29] J. W. ROWE (unpublished results).
[30] D. R. ROBERTS, *Phytochem.* **9**, 809 (1970).
[31] B. KIMLAND and T. NORIN, *Svensk Papperstidn.* (in press).

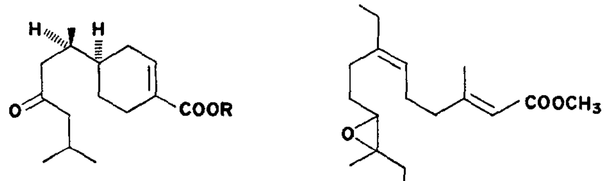
canal constituents of *P. abies*.[31] The presence of lignans and other phenolic constituents in the oleoresin may be due to the fact that they are exuded from the wounds after the cessation of the primary oleoresin.

The oleoresins and wood extractives of a few other *Picea* species have been investigated and terpenoid constituents similar to those of *Picea abies* have been found. The recently reported[32] occurrence of 24-methylenecycloartanol and the corresponding 3-ketone in *P. obovata* is of particular interest, since this constitutes the first report of triterpenes in conifer woods.

The bark extractives of some *Picea* species have been investigated.[28,33] Their characteristic constituents appear to include triterpenoids of the serratene type similar to those found in the bark of *Pinus* spp.

THE GENUS *ABIES*

Very little is known about the wood constituents of the systematically interesting firs, *Abies*, although resin acids of the abietane and pimarane types have been detected in some species.[34,35] The wood extractives[36] as well as the cortical oleoresin (Canada balsam)[37] have been investigated. Abienol (Fig. 4) is one of the main constituents of the cortical oleoresin and is significant for the properties of Canada balsam, which has some commercial importance. This compound has been isolated and/or detected in a number of other *Abies* species.[36]



R = H Todomatuic acid
Abies sachalinensis
R = CH_3 Juvabione
A. balsamea

Juvenile hormone

FIG. 8. TODOMATUIC ACID AND JUVABIONE OF *Abies* SPECIES AND THEIR STRUCTURAL RELATIONSHIP TO JUVENILE HORMONE.

Not many naturally-occurring sesquiterpene acids are known and only a few are found in conifers. The isolation and structural elucidation of the sesquiterpenoid todomatuic acid (Fig. 8) from *Abies sachaliensis* by Japanese chemists[38] were therefore of great interest. These findings became still more important in connection with the isolation and structural elucidation of the so-called 'paper factor' possessing insect juvenile hormone activity.[39] The 'paper factor' was traced to a wood constituent of Balsam fir (*Abies balsamea*) and was shown to be the methyl ester of todomatuic acid, called juvabione (Fig. 8).

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[32] A. I. LISINA, L. N. VOLSKIIJ, G. A. MAMONTOVA and V. A. PENTEGOVA, *Izv. Sib. Otd., Akad. Nauk SSSR, Ser. Khim. Nauk*, **6**, 98 (1969); *Chem. Abs.* **72**, 68403 (1970).

[33] J. H. ROGERS and L. R. ROZON, *Can. J. Chem.* **48**, 1021 (1970); and references cited therein.

[34] H. WIENHAUS and K. MUCKE, *Chem. Ber.* **75**, 1830 (1942).

[35] F. TROST, *Ann. Chim. Applicata* **26**, 38 (1936).

[36] E. P. SWAN, *Can. J. Chem.* **45**, 1588 (1967).

[37] P. S. GRAY and J. S. MILLS, *J. Chem. Soc.* 5822 (1964).

[38] M. NAKAZAKI and S. ISOE, *Bull. Chem. Soc. Japan* **34**, 741 (1961); and references cited therein.

[39] K. MORI and M. MATSUI, *Tetrahedron Letters* 2515 (1967).

An extensive study of the cortical oleoresin of a number of *Abies* species has recently been made by Zavarin and his co-workers.[40] By using advanced techniques for separation and characterization, a large number of mono- and sesquiterpenes could be identified. In *Abies magnifica*, 19 monoterpenes and 26 sesquiterpene hydrocarbons were found, including the 2 new compounds γ-humulene and cyclosativene (Fig. 5).[41] Many of these sesquiterpenes were there reported to occur in Pinales for the first time. Zavarin *et al.*[42] have extended their investigations to include some interesting chemotypes of *Abies lasiocarpa*.

There have been very few investigations of the bark, needles and other parts of various *Abies* species. However, flavonoids have been isolated[43] from the bark of *A. concolor* and from the needles of *A. amabilis*. The isolation and structural determination of abieslactone, a lanostane type of triterpene (Fig. 6) from the bark of *Abies mariesii*, *A. amabilis* and *A. procera* are of great importance.[44] This unique type of triterpene appears to be a significant Pinales bark constituent analogous to the previously mentioned serratene derivatives. Similar triterpenes have recently been found in the bark of *Pinus monticola*.[29]

THE GENUS *CEDRUS*

The wood extractives of the true cedars, *Cedrus*, appear to differ considerably from those of other Pinales species.

The heartwood and sapwood of *Cedrus atlantica* are known[45] to contain the flavonoid taxifolin and its 3′-glucoside respectively. The bark of the same species contains both of these constituents. It would be of interest to investigate more carefully the non-volatile wood constituents of *Cedrus* species to find out whether or not they contain some other phenolic constituents known from other species of the family Pinaceae.

The volatile oils of *Cedrus* species contain some interesting groups of sesquiterpenes such as the atlantones, the himachalenes and the allohimachalenes. The structure of the atlantones (Fig. 5) of *Cedrus atlantica* and *C. deodora* have recently been elucidated.[46] They are structurally related to the curcumenes, such as todomatuic acid and juvabione found in *Abies* species. They are certainly of interest in relation to compounds possessing juvenile hormone activity. The chemistry of himachalenes (Fig. 5) has been extensively investigated by Sukh Dev *et al.*[47–50] and by our own group in Stockholm.[51–53] This type of sesquiterpenes is unique, so far, to species of *Cedrus*.

The chemistry of *Cedrus* wood is unique for Pinaceae. Resin acids and related diterpenoids, characteristic for Pinaceae, have not, so far, been found in the wood. Therefore,

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[40] L. Å. SMEDMAN, K. SNAJBERK and E. ZAVARIN, *Phytochem.* **8**, 1471 (1959); and references cited therein.

[41] L. Å. SMEDMAN, E. ZAVARIN and R. TERANISHI, *Phytochem.* **8**, 1457 (1969).

[42] E. ZAVARIN, K. SNAJBERK, T. REICHERT and E. TSIEN, *Phytochem.* **9**, 377 (1970).

[43] H. L. HERGERT and E. F. KURTH, *Tappi* **36**, 137 (1953).

[44] S. UYEO, J. OKADA, S. MATSUNAGA and J. W. ROWE, *Tetrahedron* **24**, 2859 (1968); J. P. KUTNEY, N. D. WESTCOTT, F. H. ALLEN, N. W. ISAACS, O. KENNARD and W. D. S. MOTHERWELL, *Tetrahedron Letters* 3463 (1971).

[45] H. L. HERGERT and O. GOLDSCHMID, *J. Org. Chem.* **23**, 702 (1958).

[46] B. S. PANDE, S. KRISHNAPPA, S. C. BISARYA and SUKH DEV, *Tetrahedron* **27**, 841 (1971).

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we have recently studied the oleoresin exuded from the cones of *Cedrus atlantica* and *C. deodora*.[54] The composition of the cone oleoresin was found to be quite different from that of the wood oil and to contain large quantities of the common resin acids of abietane and pimarane types as well as of related diterpenoids. The composition of the oleoresin was that characteristic of Pinaceae.

The wood of most species belonging to the family Pinaceae contains resin canals but such canals are as stated above not normally occurring in *Cedrus*. Therefore, the presence of resin acids and related diterpenoids in the wood of Pinaceae appears to be confined to species and organs possessing resin canals. *Tsuga* is another species of the Pinaceae, the wood of which is lacking resin canals and as a matter of fact resin acids have not yet been isolated from the wood of *Tsuga* species.

THE GENUS *LARIX*

This genus constitutes about 10 species and the wood extractives of a few of them have been investigated in some detail. The oleoresin of European larch, *Larix decidua*, contains large amounts of resin acids of the common '*Pinus-Picea* type' but also 13-epimanool (possibly also manool) and some related diterpenoids, larixol and larixyl acetate (Fig. 4).[55,56] 13-Epimanool is also frequently occurring in the oleoresins of *Pinus* and *Picea* species. Flavonoids such as taxifolin and aromadendrin, and also lignans have been found in *Larix* species.[57–59]

It appears that some *Larix* species, *L. laricina* and *L. lyalli*, are less resiniferous than others. Resin acids and neutral diterpenoids have not been detected in these species.[59]

OTHER GENERA OF THE FAMILY PINACEAE

The genus *Pseudotsuga* is found only in the northern hemisphere. It comprises about seven species and is restricted to western North America and eastern Asia. Botanically, as well as chemically, it appears to be rather closely related to pines. The North American Douglas-fir, *P. menziesii*, is the most well-known species and has been studied from a phytochemical point of view. Two common varieties of this species are recognized, Coastal and Interior Douglas-fir, which exhibit significant differences in their wood extractive compositions.[60]

Both the heartwood and bark of Douglas-fir contain large amounts of taxifolin together with small quantities of aromadendrin, pinobanksin and pinocembrin.[61–64] No pinosylvin has been detected. The composition of the oleoresin,[65] or the so-called 'pocket resin', shows similarities to that of the pines and contains resin acids and considerable amounts of resin acid methyl esters. The main neutral constituent is thunbergol (Fig. 3),[66] structurally related

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to thunbergene, another constituent of the oleoresin. An interesting new sesquiterpene named germacrene D (Fig. 5) has recently been isolated[67] from *P. japonica*. This hydrocarbon is easily transformed into cadinane derivatives.

The hemlocks (*Tsuga*) appear to be less resiniferous. As mentioned previously, their woods lack resin canals and the presence of resin acids in the wood extractives has not been reported. Like *Picea*, however, the woods contain conidendrin.[7,68,69] Very unfortunately, the genera *Cathaya*, *Keteleeria* and *Pseudolarix* remain almost unexplored from a chemical standpoint.

CONCLUSIONS

Many species of the Pinales have been subjected to chemical investigation although some genera remain almost unexplored. A fairly large number of Pinales constituents have been isolated and structurally elucidated. However, the information available is small in comparison with that obtained from botanical studies. Nevertheless, the constituents do serve as exactly defined chemical characteristics of the relevant species and are independent of the classical taxonomic evidence. When the chemistry of Pinales has been worked out in greater detail it will prove to be a valuable complement to the biological material.

It is important for future research in this field to carry out systematic investigations on different tissues of the same species. These investigations should cover as many plant tissues as possible from each species and in some cases even individual cells. This is possible with modern techniques and some promising studies of this kind have already been carried out. Such investigations would also be extremely valuable for our knowledge about the biosynthesis of the constituents as well as their taxonomic importance.

Very little is known about the physiological properties of most plant constituents and this is also true for those of the Pinales. It is evident that studies of this type will prove to be of great value for the understanding of the complex ecological relations existing in the forest and are of interest in forestry as well as in wood science.

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