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SOME ASPECTS OF THE CHEMISTRY OF PINACEAE NEEDLES

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SUMMARY

A brief survey is given of some main classes of phenolics found in the leaves of species of the pine family (Pinaceae), with emphasis on the flavonoids. Within the limited scope of present knwowledge chemical relationships of taxonomic importance are pointed out.

1. INTRODUCTION

In the course of our work on physiological phenomena in *Larix* leaves related with phenolics (NIEMANN & NUIJTEN 1973, NIEMANN 1976), a surprising lack of knowledge of leaf-flavonoids of *Larix* species and, more general, of most Pinaceae species became apparent. This is the more striking because, from a chemotaxonomical point of view, the Pinaceae are regarded as a rather well-known family as far as the flavonoids are concerned (HEGNAUER 1962, HARBORNE 1967). This view, however, appears mainly based on the knowledge of wood constituents and to a lesser extent on that of bark of species of a limited number of genera. Economic importance partly guided the choice and thus the wood composition of *Pinus* and *Larix* and a single species of *Pseudotsuga* is well-known. Very little, however, was known of *Cedrus*, while *Keteleeria* and *Cathaya* species have practically not been investigated at all, neither for wood nor for any other part.

In larch leaves a number of flavonoids and aromatic hydroxy acids was identified (NIEMANN, NIEMANN and coworkers 1971–1976, MEDVEDEVA and coworkers 1972–1974) among which two flavonol glycosides were found which have only rarely been detected in higher plants. This is quite a contrast with the very simple *Larix* wood flavonoid composition consisting of just dihydrokaempferol (aromadendrin) and dihydroquercetin (taxifolin) (HEGNAUER 1962, HARBORNE 1967) and a trace of quercetin (NAIR & VON RUDLOFF 1959). Since long, it is recognized that within a single genus in the Pinaceae the flavonoid composition of wood, bark and leaf can be quite different (HEGNAUER 1962). It was the big difference found between the very simple flavonoid composition of wood and the complex one of needles of *Larix*, which stimulated our interest in leaf phenolics of other Pinaceae. Furthermore, the occurrence of some rare flavonols in larch needles raised the question of their eventual existence in other Pinaceae leaves. A literature survey on Pine leaf phenolics revealed a rather neglected area and the need was felt to outline the present knowledge in this field in order to be able to fill gaps in a systematic way.

2. SCOPE OF THE PRESENT STUDY

Search for leaf compounds in the Pinaceae generally can be divided into two lines of investigation. The first type of research comprises the screening of a great number of species, often for a limited number of compounds. Mainly one or more species of each genus in the pine family (or of all Gymnosperms) is involved. For flavonoids, for instance, the classic work of TAKAHASHI et al. (1960) has for several years been the most important source of information on pine needle flavonoids.

In the second type of investigations leaves of one or more species were investigated much more extensively, often in combination with investigations on physiological changes. In some cases this led to a series of publications, comprising many different classes of compounds, like the series of the Upsala group (Theander, Popoff, Norin a.o.) dealing with carbohydrates, terpenes and various phenolics like benzofuran derivatives, flavonoids and other phenylpropane derivatives from needles of *Pinus silvestris* L. (POPOFF & THEANDER 1977). Some of the following general remarks on the constituents found in the family are mainly based on screening of the first type.

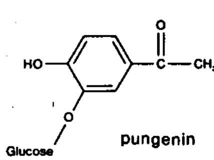
The different species hitherto investigated are treated in alphabetic order of the name of the genus. The names and classification of species and genera in the Pinaceae family used here are based on those given by Dallimore and Jackson in HARRISON's revised edition of 1966 (reprinted 1974). Thus, the Pinaceae are subdivided in the following 10 genera, comprising about 200 species: *Abies* (52), *Cathaya* (2), *Cedrus* (4), *Keteleeria* (6), *Larix* (10), *Picea* (34), *Pinus* (90), *Pseudolarix* (1), *Pseudotsuga* (5) and *Tsuga* (10). The number of species given in brackets for each genus is a rough estimate.

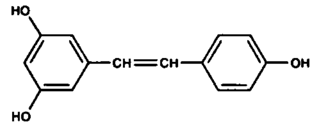
For the collection of data use was also made of previous, more general reviews like that by HEGNAUER (1962), HARBORNE (1967) and NORIN (1972). The classes of phenolics considered may arbitrarily be subdivided into 6 groups, viz. 1. the simple phenolics of the C6, C6–C1, C6–C2 and C6–C3 type, 2. the stilbenoids, 3. the phenolic acids (and coumarins), 4. the flavonoids, 5. the proanthocyanidins and other tannins, and 6. a rest group with among others the lignans. Each will be considered separately before starting with the specific chemistry of each genus.

3. SURVEY OF THE DATA

3.1. Simple phenolics

This group comprises the most simple phenols like phenol itself and resorcinol, aldehydes like *p*-hydroxybenzoic aldehyde, derivatives of acetophenone like picein and the cinnamoyl alcohols like for instance coniferyl alcohol. Of these compounds glucosides of *p*-hydroxyacetophenone (picein) and of 3,4-dihydroxyacetophenone (pungenin) or the corresponding aglycones were only found in *Abies* and *Picea* species (HEGNAUER 1962). See note 1 on p. 88.


pungenin

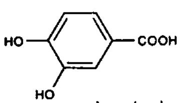

resveratrol

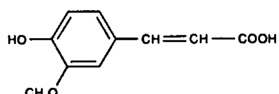
3.2. Stilbenoids

From the investigations of TAKAHASHI et al. (1960) resveratrol is the best known stilbene derivative in Pinaceae needles. It has, however, only been found in some *Abies* (2 out of 7 species investigated) and *Picea* (5 out of 11) species.

3.3. Phenolic acids and coumarins

Although benzoic and cinnamic acids like *p*-hydroxybenzoic acid, protocatechuic acid, *p*-coumaric acid and ferulic acid appear of ubiquiteous occurrence, mainly in the form of glycosides or esters, reports on these compounds in Pinaceae needles are scarce. Only recently some information became available which will be discussed under the separate genera. From a gas-chromatographic comparison for vanillic-, protocatechuic-, gallic-, syringic-, *p*-coumaric-, caffeic-, ferulic-, and chlorogenic acid, LINDNER & GRILL (1978) consider the qualitative composition of the investigated species of *Abies*, *Larix*, *Picea* and *Pinus* rather similar.

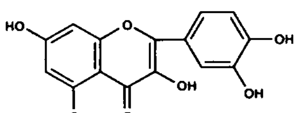

protocatechuic acid


ferulic acid

3.4. Flavonoids

Till recently, knowledge of pine leaf flavonoids was based on very few reports only describing general screenings for a certain type of compounds. Thus, SAWADA (1958) pointed to the rather outstanding place of the Pinaceae within the Gymnosperms based on the absence of biflavonyls in Pinaceae leaves, whereas the occurrence of biflavonyl formation appeared a common feature in almost all other Gymnosperm families. TAKAHASHI et al. (1960) investigated leaves of over 100 Gymnosperms (among which 68 species of the pine family) for some main flavonoid aglycones. Mainly kaempferol, quercetin and sometimes myricetin could be detected in one or more species of each genus.

Recently, the presence of C-glycosyl flavonoids was demonstrated in 6 larch species, but they were not detected in species of 8 other genera of the pine family (NIEMANN & MILLER 1975).


quercetin

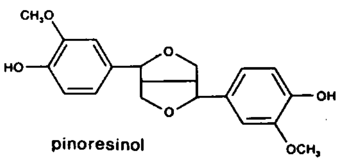
3.5. Proanthocyanidins and other tannins

According to FREUDENBERG & WEINGES (1960) the name proanthocyanidin is used for all colourless plant substances which form anthocyanidines on treatment with hot acid. The name leucoanthocyanidin is kept for the monomeric proanthocyanidins. In most older literature it is often not clear whether the 'leucocyanidins' isolated belong to the first or to the second group. The name proanthocyanidins will be used for those leucoanthocyanidins which were only specified by their acid hydrolysis product.

A general survey on proanthocyanidins in the genus *Pinus* was made by KRUGMAN (1959), who investigated 44 species which all contained proanthocyanidins giving cyanidin, and those giving delphinidin on acid hydrolysis. HIDA (1958) found mainly delphinidin-yielding proanthocyanidins in the species of the Pinaceae investigated (15 species out of 9 genera) and only incidentally the cyanidin type (5 species).

3.6. Lignans and other phenolics

Unlike the wood, from which lignans as for instance pinoresinol have been known for a long period, pine leaves till recently have not been reported as a source of lignans (HEGNAUER 1962). At this moment one report is known on the occurrence of different lignans like liovil, lariciresinol, pinoresinol, matairesinol, and isolariciresinol in needles of species of *Abies*, *Picea*, *Larix* and *Pinus* (TJUKAVKINA et al. 1977).



pinoresinol

For other compounds in this section too only incidental reports on for instance dilignols or diterpene-phenolics exist, which will be discussed under the different genera.

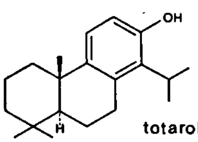
3.7. The genus *Abies*

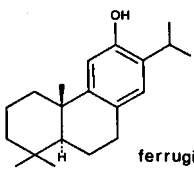
For such a relatively large genus only a few species have been investigated in some detail. Vanillic-, gallic-, syringic-, *p*-coumaric-, caffeic-, ferulic-, and chlorogenic acid were found in *Abies alba* (LINDNER & GRILL 1978). TAKAHASHI et al. (1960) found quercetin in 6 species (out of 6 investigated), kaempferol in 4 and myricetin in 2 (all of the same 6 species). HERGERT & GOLDSCHMID (1958) found dihydroquercetin-3'-glucoside in leaves of the pacific silver fir (*Abies amabilis* (Dougl.) Forbes). They considered the leaf to be the site of synthesis of this compound, from where it is assumed to be translocated to the heartwood and outer bark and deposited as the aglycone. The best investigated species are *A. nephrolepis* Maxim. and *A. sibirica* Ledeb. from which glycosides (β-glucosides) and/or free aglycones were isolated of *p*-hydroxybenzoic acid, vanillic acid, protocatechuic acid and *p*-coumaric acid (MEDVEDEVA et al. 1974c, 1977b), 8 flavonoids were identified as: kaempferol, quercetin, their 3- and 7-glucosides, isorhamnetin-3-glucoside and apigenin-8-C-glucorhamnoside (MEDVEDEVA et al. 1974b), and some lignans were identified (by co-chromatography only!) as: liviol, lariciresinol, matairesinol and isolariciresinol (from both species) and pinoresinol and hydroxymatairesinol (from *A. nephrolepis* only) (TJUKAVKINA et al. 1977).

3.8. *Cathaya, Cedrus* and *Keteleeria*

Species in these genera have not or only superficially been investigated in general screenings. TAKAHASHI et al. (1960) identified kaempferol from *Keteleeria davidiana* Beiss. and found no flavonoid aglycones in *Cedrus deodara* Loud. leaves. Main C-glycoflavones were not detected in *Cedrus libani* A. Rich. and *Keteleeria fortunei* (A. Murr.) Carr. (NIEMANN & MILLER 1975). The two *Cathaya* species were not investigated at all. Research, recently started for flavonoids in *Cedrus libani* and *C. deodara* indicated the presence of a complex mixture of flavonol glycosides (Van Genderen & Van Schaik, in preparation and unpublished data). Leaves of *Cedrus atlantica* (Endl.) Carr. cv glauca contained among others the rare flavonols laricitrin (3'-methylmyricetin) and syringetin (NIEMANN 1977) which were also found in all *Larix* species investigated hitherto.

Minor concentrations of two diterpenephenolics were found in leaves of *Cedrus atlantica* Mam. and identified as totarol and ferruginol (LERCKER et al. 1977).

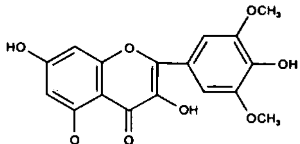




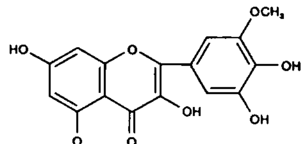
3.9. *Larix*

Larix is the best known genus. Of the 10 species *Larix decidua* Mill., *L. gmelinii* (Rupr.) Kuzeneva (= *L. dahurica* Turcz. ex Traut.), *L. griffithii* Hook., *L. leptolepis* (Sieb. et Zucc.) Gord. (= *L. kaempferi* (Lamb.) Carr.), *L. laricina* (Du Roi) K. Koch, *L. lyallii* Parl., *L. mastersiana* Rehd. & Wils., *L. occidentalis* Nutt., *L. potanini* Batalin H. S., and *L. sibirica* Ledeb. (= *L. russica* (Endl.) Sab. ex Traut.), five have been investigated in detail. Not much is known of the simple phenolics, only *p*-hydroxybenzaldehyde and vanillin were isolated from *L. laricina* needles (NIEMANN 1972), but for the phenolic acids and flavonoids a great similarity in composition became apparent. Thus, *L. decidua* (NIEMANN 1975a), *L. gmelinii* (TJUKAVKINA et al. 1975, NIEMANN 1975b), *L. leptolepis* (NIEMANN 1973, 1974, NOMURA 1976, NOMURA & MUTO 1976), *L. laricina* (NIEMANN & BEKOOY 1971, NIEMANN 1972) and *L. sibirica* (MEDVEDEVA et al. 1972a, 1972b, 1972c, 1973, 1974a, TJUKAVKINA et al. 1974) all exhibit a similar pattern of flavonoids, characterized by mono-, di- and tri-hydroxylation of the B-ring.

Data of the Irkutsk group and ours have been summarized in *table 1*, to which some of our unpublished results were added. From this table it appears that in addition to the common flavonol glycosides also rare compounds like syringetin and laricitrin (3'-methylmyricetin) were found in the five more intensively investigated species.



syringetin



laricitrin

So far, syringetin has only been found in *Lathyrus pratensis* (HARBORNE 1965), *Soymida februfuga* (PARDHASARDI & SIDHU 1972), *Philydrum lanuginosum* (BOHM & COLLINS 1975), *Limnanthus douglasii* and other *Limnanthus* species (PARKER & BOHM 1975), *Heuchera micrantha* (WILKINS & BOHM 1976), *Cedrus atlantica* (NIEMANN 1977), *Dorycnium suffruticosum* and *Tetragonolobus siloquosus* (JAY et al. 1978) and *Pinus jeffreyi* (NIEMANN 1978a). Laricitrin, first

Table 1. Phenolic acids and flavonoids hitherto isolated from *Larix* needles*.

	L. decidua	L. gmelinii = L. dahurica	L. leptolepis	L. laricina	L. occidentalis	L. sibirica
p-hydroxybenzoic acid	+	+	+	+		+
vanillic acid	+	+	+	+		+
syringic acid		+	+			+
protocatechuic acid	−	−	+			−
p-coumaric acid	±	+	+	+		+
ferulic acid	+	−	+	tr		−
kaempferol	+	+	+	+	+	+
quercetin	+	+	+	+		+
isorhamnetin	+	+	+	+	+	+
myricetin	+	+	+	+		+
laricitrin	+	+	+	+		+
syringetin	+	+	+	+	+	+
dihydroquercetin			+		+	
naringenin			+			
apigenin	+	+				
vitexin	+	+	+	+	+	+
kaempferol-3-(*p*-coumarylglucoside)	+	+	+	+	+	+

* Most flavonols were found as 3-glucosides or 3-rutinosides, naringenin and apigenin as 7-glucosides, vitexin as such or as its 8-(glucosyl)xyloside or rhamnoside, the phenolic acids occur mainly as the β-glucosides. Unpublished results on L. gmelinii, L. laricina and L. occidentalis were added.

isolated from larch-needles (NIEMANN 1972, 1973, TJUKAVKINA et al. 1974) has later also been found together with syringetin in *Limnanthus* (PARKER & BOHM 1975), *Heuchera* (WILKINS & BOHM 1976), *Cedrus* (NIEMANN 1977), *Tetragonolobus* (JAY et al. 1978) and *Pinus* (NIEMANN 1978a).

In addition to the phenolic acids mentioned in *table 1*, LINDNER & GRILL (1978) also found syringic-, protocatechuic-, gallic-, caffeic-, and chlorogenic acid in *L. decidua* needles.

Whereas glycosidation of the larch flavonols mainly occurs in position 3 and glucosides and rutinosides prevail, another feature of the larch needles is the presence of acylated flavonol glucosides. Kaempferol-3-(*p*-coumarylglucoside) was isolated from all 6 species *(table 1)*, in which it occurs in comparatively high concentrations. Acylation with *p*-coumaric acid and ferulic acid, however, appears a very common phenomenon and trace amounts of acylated flavonoid glycosides have been found for almost all aglycones mentioned in *table 1* (NIEMANN 1975c, 1978b).

In *L. leptolepis* not only flavonols, flavones, C-glycoflavones and flavanones occur (NIEMANN 1976), but also catechin, epiafzelechin and possibly eriodictyol (NOMURA 1976). Of proanthocyanidins very little is known; one such compound leading to delphinidin on hydrolysis, was found in *L. leptolepis* needles (HIDA 1958). In our work, however, the main proanthocyanidin in this species appeared of the cyanidin type (NIEMANN 1976).

Lignans were found in both *L. sibirica* (6) and *L. dahurica* (8) (TJUKAVKINA et al. 1977), identified by co-chromatography as secoisolariciresinol, liovil, lariciresinol, olivil, pinoresinol, matairesinol, isolariciresinol and α-conidendrin.

It should be emphasized that the similarity in flavonoid (and phenolic acid) composition in larch species only exists in a qualitative way. Considered quantitatively compositions are often much more apart (NIEMANN & KOERSELMAN-KOOY 1977). Most characteristic in larch needles are the methylated derivatives laricitrin and syringetin. A corresponding hydroxylation/methylation pattern was, however, not found in the phenolic acid glycosides. Only syringic acid was found in a few species *(table 1)*, and a supposed sinapylglucoside in *L. leptolepis* (Niemann, unpublished), but 3'-methoxy-4,5-dihydroxy-compounds were never detected. Also in wood, lignans or benzoic or cinnamic aldehydes with a corresponding substitution type, have not been found (GITTARD & SCHOENTAL 1969, TJUKAVKINA et al. 1974).

3.10. *Picea*

For this relatively large genus little is known of the leaf phenolics. DITTRICH (1970) demonstrated the presence of *p*-hydroxybenzoic acid glucoside in needles of *Picea abies* L. and *P. mariana* Mill. and of *o*-coumarylglucose in *P. abies*. LINDNER & GRILL (1978) found free protocatechuic-, vanillic-, gallic-, syringic-, *p*-coumaric-, caffeic-, ferulic-, and chlorogenic acid in the same species. The occurrence of the *β*-glucoside of *p*-hydroxybenzoic acid was shown in two other species (*P. obovata* R. Mayr. and *P. koraiensis* Nakay) together with the glucosides of vanillic- and *p*-coumaric acid, whereas protocatechuic acid and its glucoside were only found in *P.koraiensis* and ferulic acid and its glucoside only in *P. obovata* (MEDVEDEVA et al. 1977b). Coniferin which accumulates in stem and root, could not be detected in needles of *P. abies* (MARCINOWSKI & GRISEBACH 1977).

Up to the early sixties acetophenone derivatives (picein, pungenin and/or their aglycones) were found in 8 *Picea* species (HEGNAUER 1962), since then the occurrence of picein and/or its aglycone was again demonstrated in *P. abies* (DITTRICH 1970, ESTERBAUER et al. 1975) and in *P. obovata* (IVANOVA et al. 1976), whereas pungenin was found in *P. mariana* (DITTRICH 1970). In addition to picein IVANOVA et al. (1976) also isolated pungenin and the glucoside of 4-hydroxy-3-methoxyacetophenone from *P. obovata*, which is the first report of the latter compound in *Picea*.

Of the stilbenoids the occurrence of resveratrol in *Picea* species was already mentioned in the general part. ITO (1961) indicates a differences in the sections *Omorika* and *Eupicea* of the genus *Picea* based on the occurrence of the leaf stilbenoids resveratrol and an unidentified one (together with piceol and pungenigenin) in *P. bicolor* Mayr in *Omorika* and their absence in *Eupicea* species. DITTRICH (1970), DITTRICH & KANDLER (1971) identified piceatannolglucoside (3, 4, 3', 5'-tetrahydroxystilbene glucoside) and isorphapontin (3, 5, 4'-trihydroxy-3'-0-methylstilbene glucoside) in needles of *P. abies* and *P. mariana*, whereas FORREST (1975a) found low concentrations of the four main stem stilbenes of *P. sitchensis* (Bong.) Carr. (astringin, isorhapontin, astringenin and isorhapontigenin) in its leaves.

Of the flavonoids, kaempferol and quercetin glucosides were identified in *P. abies* and *P. mariana* (DITTRICH 1970) and *P. sitchensis* (FORREST 1975a). TAKAHASHI et al. (1960) found only kaempferol in *P. maximowiczii* Regel. needles and no aglycones in 10 other *Picea* species. Main C-glycoflavones were not detected in *P. breweriana* S. Watson (NIEMANN & MILLER 1975). HERGERT & GOLDSCHMID (1958) found dihydroquercetin-3'-glucoside in *P.sitchensis*. *P. ajanensis* Fisch. was investigated in more detail, IVANOVA et al. (1975) found naringenin, aromadendrin (= dihydrokaempferol), kaempferol, quercetin and apigenin. Recently, in a series of publications of O-acylated flavonoid glycosides in Pinaceae needles, the occurrence of these compounds in *P. koraiensis* was reported (IVANOVA et al., 1978a).

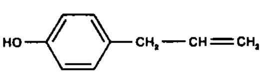
Anthocyanins were isolated from young leaves and identified as cyanidin-3-glucoside in *P. glauca* (Moench) Voss., *P. montigena* Mast. and in some hybrids, whereas in addition to the cyanidin glucoside also delphinidin-3-glucoside was found in the hybrid *P. glauca* × *jezoensis hondensis* (SATAMOUR 1967).

In addition to the flavonoids, proanthocyanidins belong to the main leaf components of *P. sitchensis* in which not less than 15 would be present together with epicatechin and catechin (FORREST 1975a). Catechin, epicatechin and gallocatechin were also found in *P. abies* and *P. mariana* (DITTRICH 1970).

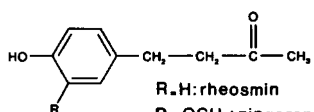
Lignans have only recently been found in leaves of *P. obovata*, *P. koraiensis* and *P. ajanensis*, in most species secoisolariciresinol, liovil, lariciresinol, olivil, pinoresinol, matairesinol, hydroxymatairesinol, a trace of ketomatairesinol and isolariciresinol was identified (TJUKAVKINA et al. 1977).

3.11 *Pinus*

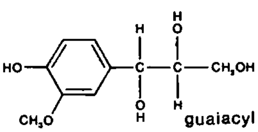
This large genus (around 90 species) is well-known for its wood polyphenolics, but needles of only very few species have been investigated in some detail. Only recently a number of interesting compounds was isolated from *Pinus contorta* Doug. (Coastal) and *P. silvestris* L. Whereas the main stem phenolic coniferin is generally not detected in the needles its dihydro analogue was found in needles of *P. contorta*, together with the γ glucoside of dihydroconiferyl alcohol, the 4 and γ glucosides of dihydro-*p*-coumaryl alcohol and glucosides of chavicol and the phenylbetan-2-ones zingerone and rheosmin (HIGUCHI et al. 1977a and b).



chavicol



R.H: rheosmin
R - OCH_3: zingerone



guaiacyl glycerol

Another interesting compound, isolated from *P. silvestris* needles is threo-guaiacyl glycerol, found both in its free form and with glucose at the α- or β-position (THEANDER 1965).

Phenolic acids, caffeic-, homoprotocatechuic- and chlorogenic acid were first isolated from *P. silvestris* (KOWALSKA 1971b). MEDVEDEVA et al. (1977b) added the glucosides and/or free form of *p*-hydroxybenzoic-, vanillic-, protocatechuic-, *p*-coumaric- and ferulic acid for the same tree, and also (with the exception of protocatechuic acid) for *P. sibirica* R. Mayr. From *P. silvestris*, *P. cembra* L. *P. nigra* Arnold and *P. mugo* Turra, LINDNER & GRILL (1978) identified the free acids: protocatechuic-, vanillic-, gallic-, syringic-, *p*-coumaric, caffeic-, ferulic-, and chlorogenic acid.

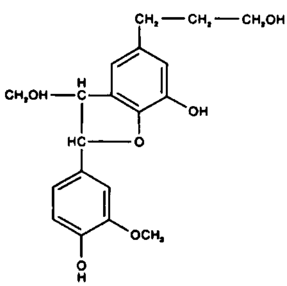
Of the leaf flavonoids SAWADA (1958) did not find biflavonoids in 23 species, no main C-glycoflavonoids were found in *P. silvestris* and *P. jeffreyi* Grev. & Balf. (NIEMANN & MILLER 1975). TAKAHASHI et al. (1960) mainly found kaempferol and quercetin and sometimes myricetin or dihydroquercetin in 42 species. Naringenin was found in chloroplasts of *P. nigra* Arnold (SAUNDERS & MCCLURE 1976). From *P. silvestris* quercetin- and dihydroquercetin-3-glucoside (POPOFF & THEANDER 1977), quercetin-7-glucoside (KOWALSKA 1971a), sylpin (5, 6, 4'-trihydroxy-3-methoxy-8-methylflavone) (MEDVEDEVA et al. 1977a), acylated flavonol glycosides (ZAPESOCHNAJA et al. 1978a) and 3"-0-*p*-coumarylisoquercitrin (IVANOVA et al. 1978b), and di-*p*-coumaryltrifolin (ZAPESOCHNAJA et al. 1978b) were isolated. KOWALSKA (1970, 1971a) suggested the presence of two biflavonoids but this observation has never been confirmed.

Acylated flavonol glucosides, together with 6-methylkaempferol-3-glucoside, were found in *P. contorta* (HIGUCHI & DONNELLY 1978). An A-ring methylated kaempferol derivative, probably identical with the latter, was also isolated from *P. jeffreyi* needles, together with acylated flavonol glucosides and glycosides of kaempferol, quercetin, isorhamnetin, myricetin, laricitrin and syringetin (NIEMANN 1978a). An anthocyanin was found in young seedlings (inclusive needles) of *P. lambertiana* Dougl. and identified as malvin (KRUGMAN 1956).

The proanthocyanidins found throughout the genus were discussed before. Catechins were isolated from *P. silvestris* (catechin, POPOFF & THEANDER 1977) and *P. sibirica*. From needles of the latter SHUMAILOVA (1971) identified catechin, epigallocatechin, gallocatechin, epicatechin, epigallocatechin gallate and epicatechin gallate.

Lignans were found in *P. silvestris*, from which POPOFF & THEANDER (1977) isolated glycosides of isolariciresinol and secoisolariciresinol. In addition to the aglycones of those two compounds TJUKAVKINA et al. (1977) also identified liovil, lariciresinol, olivil, pinoresinol and matairesinol from *P. silvestris* and *P. sibirica*.

From both *P. silvestris* and *P. contorta* glycosides of a dilignol, 2,3-dihydro-7-hydroxy-2(4'-hydroxy-3'-methoxyphenyl)-3-hydroxymethyl-5-benzofuranpropanol, were isolated (POPOFF & THEANDEr 1975, 1977; HIGUCHI et al. 1977).



3.12. *Pseudolarix*, *Pseudotsuga* and *Tsuga*

TAKAHASHI et al. (1960) reported quercetin and kaempferol for *Pseudolarix kaempferi* Gordon (= *P. amabilis* (J. Nels) Rehd.), the same aglycones plus myricetin for *Pseudotsuga japonica* Beiss. and kaempferol for two out of three *Tsuga* species. Main C-glycoflavones were not detected in *Pseudolarix amabilis*, *Pseudotsuga menziesii* (Mitbel) Franco and *Tsuga chinensis* (Franch.) Britzel (NIEMANN & MILLER 1975). *Pseudolarix amabilis* has been investigated for main leaf flavonoids in our laboratory and appeared to contain one principal flavonoid, myricetin-3-rhamnoside, whereas kaempferol-, and myricetin-3-glucoside, quercetin-3-rhamnoside and acylated kaempferol-3-glucoside were present in much lower concentration (NIEMANN 1975d). HIDA (1958) found high concentrations of delphinidin and traces of cyanidin in the autumn-coloured leaves of the same tree, HERGERT and GOLDSCHMID (1958) found dihydroquercetin-3'-

glucoside in *Tsuga heterophylla* Sargent and the same compound and quercetin-3'-glucoside in Douglas fir needles *(Pseudotsuga menziesii)*.

3.13 Seasonal variation and geographic differentiation

Comparison of plant species based on leaf constituents has to be done with extra care because of the rapid turnover possible in these organs. Actually, collection dates and special physiological conditions should always be included in chemotaxonomic articles. As far as seasonal variation is concerned the few publications on pine leaf-flavonoids mainly point to an active metabolism in young developing leaves, followed by a more stable situation in full-grown leaves, often with a gradual decline in concentration at the end of the season. Thus, DITTRICH (1970) found kaempferol-3-glucoside (K3G) and quercetin-3-glucoside (Q3G) only in young *Picea* needles and not in old ones, kaempferol-7-glucoside (K7G) was also found in older needles, be it in very low concentration. In tracer experiments synthesis of K3G and Q3G was found at the start of May (München) in young needles, still soft and yellow-green, and at 60% of their maximum fresh weight. Two days later, however, a decline in concentration started and on June 9 K3G, and September 10 Q3G, could no longer be detected. Synthesis of K7G had already stopped before the first experiment (May 2), but decrease in concentration was very slow and K7G could still be detected in one and two-year-old needles. In *Larix* needles an optimum concentration of K3G and Q3G was found at the end March (Utrecht) followed by a decline and a more stable situation for full-grown needles (NIEMANN 1976). NOMURA (1976) found a rather stable situation for K3G in larch needles between June 1st and November 1st (Sapporo) with a slight increase in autumn. In annual shoots K3G disappeared in summer and was replaced by kaempferol.

Similarly, for the acetophenones pungenin, in *Picea pungens*, NEISH (1958), and for picein in *P. abies* ESTERBAUER et al. (1975) demonstrated the occurrence of an annual rhythm with maximum values in spring and summer respectively. In DITTRICHS (1970) experiments synthesis of picein and of the stilbene glucosides piceatannol glucoside and isorhapontin in *P. abies* needles only started when the flavonols not only were no longer synthesized but already being broken down. In general, it seems necessary to investigate both young and full-grown leaves for a complete insight in leaf phenolics, although in several cases those compounds present in young leaves can also be detected in older ones.

A much greater variety was found between bud and needle stages of *Larix leptolepis* (NIEMANN 1976). Main needle flavonoids like kaempferol-3-(*p*-coumarylglucoside), were not detected at all (or only in very small concentration) in bud stages, whereas a main bud compound like dihydroquercetin disappeared rapidly during bud break. In addition to seasonal variation, VARAKSINA (1973) also found a diurnal variation in the quantities of 5 flavonoids of *Larix sibirica*. For picein in *Picea abies* almost no influence of a daily rhythm on the concentration was found (ESTERBAUER et al. 1975).

Much less information exists on geographic variation of phenolic constituents in species of Pinaceae. Wellendorf and co-workers (WELLENDORF et al. 1971, KAUFMANN et al. 1974) reported quantitative variation in a number of unidentified fluorescent phenolic compounds in *Picea abies* needles from 3 geographically separated populations. FORREST (1975c) found the use of phenolic concentration of limited value for separating provenances for *Picea sitchensis* with stilbene levels and total proanthocyanidin as most informative characteristics. Large variation between individual trees and between various growing sites obscured the effects. High variation between trees was also found by ESTERBAUER et al. (1975) for the picein and *p*-hydroxyacetophenone content of *Picea abies* needles; differences went as far as a 60 fold amount of *p*-hydroxyacetophenone found in one tree towards another (expressed in mg/g fresh weight). For *Larix* NIEMANN & BAAS (1978) found a very large variation in the flavonoid content of seedling needles due to difference in genotype.

4. DISCUSSION

Considering the present knowledge on pine leaf phenolics, the most striking point is the lack of it. Only incidentally a few species of a genus have been investigated in detail for a certain type of phenolics. Actually, a comparison for common properties in this area seems only possible after filling many existing gaps. Up to now, one of the most important aspects of pine leaf flavonoids considered from a taxonomic point of view, was the absence of biflavonoids in the Pinaceae. The finding of biflavonoids in *Pinus silvestris* needles by KOWALSKA (1970, 1971a) at the moment does not seem to change this aspect since hitherto no confirmation of her work could be obtained.

From TAKASHI and coworkers screening (1960) the occurrence of an array of flavonoids in pine needles was already demonstrated. The few more extensive investigations given since confirm and extend in all species investigated the conception of Pinaceae as 'pronounced accumulators of flavonoids' (HEGNAUER 1962). Owing to the very limited number of investigations any special trend, either in a genus, or in the whole family, can hardly be recognized. A few items in flavonoid chemistry seem worth considering for a possible taxonomic value, the occurrence of methylated myricetin derivatives, that of C-methylflavonoids and possibly that of a range of acylated flavonol glycosides.

Syringetin and/or laricitrin glycosides have so far rarely been found and thus their occurrence in *Larix*, *Cedrus* and *Pinus* species might indicate some interconnection. The lack of corresponding phenolic acids or aldehydes in *Larix* may point to an active flavonol B-ring methylating enzyme system present in needles of some genera but absent in for instance *Pseudolarix*. The fact that the few Angiosperms in which these compounds have been found belong to very diverse families diminishes their value as a taxonomic marker of the family. Possibly also, lack of recognition of a hitherto unknown or badly known group of compounds plays a rôle in this connection. The methylated myricetin derivatives may be much more common than nowadays supposed. On the other hand, the bright UV-fluorescence of the underlying compounds observed on chromatograms, seems in contradiction with such a view.

In *Pinus* species C-methylflavonols have now also been found in needles, and although up to now only three reports exist, needle composition in this respect reflects pine heartwood and bark composition (HARBORNE 1967).

Acylated flavonol glycosides have now been reported in *Cedrus*, *Larix*, *Picea*, *Pinus* and *Pseudolarix* whereas species in the other genera remained uninvestigated in this respect. Although these compounds have not so often been reported in plants, I am convinced (see also Niemann 1978b) of their ubiquitous occurrence, and therefore of their limited taxonomic value. The only aspect which may be of significance is the relatively high attribution to the phenolic content we observed in the HPLC chromatograms of *Cedrus* (NIEMANN 1977) and *Pinus* (NIEMANN 1978a).

Interesting is the occurrence of acetophenone and stilbene derivatives in *Abies* and *Picea* species, a type of compounds which has possibly been replaced in *Pinus* by phenylpropene or phenylbutanone derivatives. Again, however, the number of reports is far too scarce for any conclusions. See note 1, p. 88.

Summarizing: although the last years added a sufficient number of data to expect a rich array of all types of phenolics in needles of Pinaceae, any conclusion on the possible evolutionary relationships between the Pinaceae genera based on pathways in phenol synthesis, requires knowledge of a much wider scope than at present available.

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Notes added in proof

1. Contrary to earlier reports, *p*-hydroxyacetophenone has recently also been isolated from *Larix* and *Pinus* species (IVANOVA et al., 1978c).

2. PARKER et al. (in press) isolated glycosides of kaempferol, quercetin, isorhamnetin, myricetin, laricitrin and syringetin from needles of *Abies amabilis* (D. Douglas) J. Forbes. In addition to 3-glucosides and 3-rutinosides, also 3-rhamnosides and 3-galactosides were found. Many more flavonoids were present of which rhamnosylvitexin and dihydroquercetin were identified. Laricitrin and syringetin glycosides also were found in needles of *A. balsamea*, *A. grandis*, *A. lasiocarpa* and *A. magnifica* (Parker, personal communication).

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