

Constituents of Pine Heartwood

XXVIII.* Investigation of Four additional *Pinus* species by Paper Partition Chromatography

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Part XXV of this series¹ described the results of an investigation, by paper chromatographic methods, of forty-eight *Pinus* species, representing twelve of the thirteen groups into which the genus is divided in Shaw's system². The group which was not represented was *Gerardianæ* (subgenus *Haploxylon*, subsection *Paracembra*), consisting of two species, *P. Bungeana* Zucc. from China, and *P. Gerardiana* Wall. from the Himalayas. We have now obtained heartwood samples of both these species, and of two other species not previously investigated, *P. longifolia* Roxb. from the Himalayas and *P. formosana* Hayata from Formosa. These four species have been investigated by the methods described in Part XXV¹ and the results are summarised in Table 1.

The two species from the group *Gerardianæ* contain a combination of heartwood phenols not found in any other pines hitherto investigated. In contrast to all the other pines from the subgenus *Haploxylon* they do not contain any flavones (chrysin or tectochrysin), nor any dibenzyls (dihydropinosylvin or its monomethyl ether). They contain the four most common heartwood phenols, pinosylvin and its monomethyl ether, pinocembrin and pinobanksin together with pinostrobin and strobobanksin. The last-mentioned substance is a flavanone containing a methylphloroglucinol nucleus³, and phenols of this type (strobopinin, cryptostrobin, strobochrysin and strobobanksin) have hitherto only been found in pines belonging to the group *Strobi*⁴. As judged from the intensity of the spots on the chromatogram, the content of strobobanksin is rather high. In addition, strobopinin and probably also cryptostrobin have been found in *P. Bungeana* but not in *P. Gerardiana*. Strobo-

* XXVII. *Svensk Papperstidn.* 54 (1951) 275.

Table 1. Heartwood constituents of four *Pinus* species.Symbols and abbreviations, see Part XXV¹.

Species	Pinosylvin	PSM	DHPS	DHPSM	Pinocembrin	Chrysin	Pinostrobin	Tecto-chrysin	Pinobanksin	Strobo-banksin	Strobopinin	Crypto-strobin
A. Haploxyton												
Subsection <i>Cembra</i> , group <i>Strobi</i> :												
<i>P. formosana</i> Hayata	+	+	?	+	+	+	+	—	+	+	—	—
Subsection <i>Paracembra</i> , group <i>Gerardianae</i> :												
<i>P. Bungeana</i> Zucc.	+	+	—	—	+	—	+	—	+	+	+	?
<i>P. Gerardiana</i> Wall.	+	+	—	—	+	—	+	—	+	+	—	—
B. Diploxyton												
Subsection <i>Parapinaster</i> , group <i>Longifoliae</i>												
<i>P. longifolia</i> Roxb.	+	—	—	—	+	—	—	—	+	—	—	—

None of the unknown fluorescent compounds D—G (see Part XXV¹) have been found in these species.

chrysin can not be satisfactorily identified on paper chromatograms by the method used here¹.

Thus, the pines belonging to the group *Gerardianae* seem to be unable to hydrogenate stilbenes to dibenzyls or to dehydrogenate flavanones to flavones. These two reactions, probably connected in some way, are characteristic of the other pines of the subgenus *Haploxyton*⁴. On the other hand, the group *Gerardianae* is distinguished from the subgenus *Diploxyton* by the occurrence of pinostrobin and C-methylflavanones. From a chemical standpoint, therefore, it would be justified to regard *Gerardianae* as a third subgenus of the genus *Pinus*. It may be mentioned here that two samples of *P. Gerardiana* and one of *P. Bungeana* have been investigated.

Of the other two pine species investigated, *P. formosana* is very closely related to *P. parviflora*, which has been previously studied¹. *P. formosana* contains pinostrobin and strobobanksin, which have not been found in *P. parviflora*, but the latter species, however, contains two other C-methylflavanones, strobopinin and cryptostrobin.

Finally, the composition of the heartwood extract from *P. longifolia* has one striking feature — the complete absence of pinosylvin monomethyl ether. *P. canariensis*, the pine which is most closely related to *P. longifolia*, contains that compound, as do all the other *Diploxylon* pines hitherto investigated¹.

EXPERIMENTAL

The methods used for the analysis of the heartwood extracts were those described in Part XXV¹.

SUMMARY

The heartwoods of *Pinus Bungeana* Zucc. and *Pinus Gerardiana* Wall. contain stilbenes and flavanones, including C-methylflavanones, but none of the flavones or dibenzyls which have been found in all other pines from the subgenus *Haploxylon*.

The heartwood constituents of *Pinus formosana* Hayata and *Pinus longifolia* Roxb. are those which could be expected from a taxonomic standpoint, expect that *P. longifolia* does not contain any pinosylvin monomethyl ether.

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