

The Chemistry of the Natural
Order Cupressales. XV*. Heart-
wood Constituents of *Austrocedrus*
chilensis (D. Don), Florin et Bou-
telje (= *Libocedrus chilensis*
(D. Don) Endl.)

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Most of the genera of the family Cupres-
saceae belong either to the northern or to
the southern hemisphere but one; *Libo-
cedrus sensu lato* has a strange distribution,
occurring along the coasts of the whole
Pacific.

According to modern botanical views this
genus, however, does not constitute a
natural group and at present the following
genera are recognised: *Heyderia* (northern
hemisphere), *Pilgerodendron*, *Austrocedrus*,
Papuacedrus and *Libocedrus sensu stricto*
(all southern hemisphere).

Recently Corbett and Wright¹ reported
that they had been unable to isolate any
characteristic heartwood constituents from
Libocedrus Bidwillii Hook. (*L. s. str.*),
New Zealand, which is in agreement with
unpublished results from this laboratory.
(Similar results were also obtained with the
Tasmanian *Diselma Archeri* Hook. fil. also
of the Cupressaceae — B. Thomas, un-
published).

Zavarin and Anderson² found in the
Californian *Heyderia decurrens* (Torr.) K.
Koch (*Libocedrus decurrens* Torr.) carva-
rol, hydrothymoquinone, thymoquinone,
the two hydrothymoquinone monomethyl
ethers, libocedrol (which is a dehydrogena-
tion product of one of them) and (Dr.
Anderson, private communication) β -thuja-
plicin. *Heyderia*, therefore shows certain
chemical affinities to the northern *Tetra-
clinis* from which Grimal³ isolated the
three first mentioned compounds but
which, generally, has been regarded to be
related to a southern tribe of the Cupres-

saceae. The East Asian *Heyderia formosana*
(Florin) Li (= *Libocedrus formosana* Flo-
rin) which was studied some time ago by
Ishikawa⁴, apparently, differs consider-
ably from *H. decurrens* containing mainly
a series of highly interesting terpenoid
acids among which shonanin acid is the best
known. The presence of unidentified
"phenols" was also reported.

We have now examined the heartwood
of *Austrocedrus chilensis* (D. Don) Florin et
Boutelje (*Libocedrus chilensis* D. Don)
which is endemic to Chile and constitutes
the sole recent species of the genus *Austro-
cedrus*. Taxifolin and β -thujaplicin were
isolated. This is the first instance of a tro-
poloniferous member of the family Cupres-
saceae occurring in the southern hemi-
sphere. The yield of β -thujaplicin was un-
expectedly high (over two per cent) and
the wood, therefore, constitutes a rich
source of this tropolone. As one would
expect considering the fact that the "phe-
nol coefficient" of β -thujaplicin⁵ is over
100, the wood is extremely durable and
resistant to the attack of wood destroying
fungi (Docent E. Rennerfelt, private com-
munication).

Experimental. 1. *Extraction with acetone.*
The powdered heartwood (1 240 g) was extrac-
ted continuously for three days with acetone.
The soluble material (151 g) was shaken three
times with ether (500 ml portions) yielding an
ether soluble fraction (79 g), "A". The residue
was boiled twice with water (300 ml portions)
for 15 minutes and the combined extracts
treated with animal charcoal, cooled and sha-
ken with ether. The ether solution was dried
over sodium sulphate and the ether removed.
The residue was boiled with chloroform (10 ml)
and the solution cooled when taxifolin (1 g)
crystallised. Solution A was evaporated to
dryness and the residue boiled with ligroin
(b. p. 90—120°) (3 \times 500 ml) when 38 g ma-
terial passed into solution ("B") leaving an
insoluble residue (41 g) which was worked up
like A employing, however, 30 ml of chloro-
form. 3 g Taxifolin was isolated followed by a
second crop (0.3 g) on concentration of the
mother liquor. Total yield of crude taxifolin
4.3 g (0.35 %). It was purified by recrystalli-
sation from water, m. p. 238—239°, (not de-
pressed on admixture with an authentic speci-
men), $[\alpha]_D^{24}$ 47° (acetone-water 1:1, c 1.03). The
purity of the substance as well as the absence
of aromadendrin in the mother liquors was
demonstrated by paperchromatography em-

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ploying 1) neutral paper, 2) boric acid impregnated paper, and as developers 1) hypophase of chloroform, ethanol, water (8:2:1) and 2) epiphase of benzene, ethanol and boric acid saturated water (6:2:1). Only a single spot corresponding to that of taxifolin was observed on spraying with bisdiazotised benzidine.

The ligroin solution B was evaporated and the residue dissolved in ether (700 ml) and shaken successively with a saturated aqueous solution of sodium bicarbonate (3 × 200 ml), a 10 % sodium carbonate solution (4 × 300 ml) and a 5 % potassium hydroxide solution (3 × 200 ml). Evaporation of the residual ether solution yielded a neutral fraction (6 g) which was subjected to distillation with steam. Only about one gram of a terpene-like volatile oil was obtained and a semisolid non-volatile fraction which were not further investigated.

Acidification and ether extraction of the aqueous solutions yielded a bicarbonate soluble fraction (1.1 g), a "carbonate fraction" (26 g) and an "alkalifraction" (1.8 g) of which only the carbonate fraction was investigated. It crystallised readily and yielded after recrystallisation from light petroleum (b. p. 40–60°) pure β -thujaplicin (25.8 g, 2.2 %) m. p. 52.5–53° (mixed m. p.). Cu-complex: from chloroform crystals m. p. 93–94° (containing solvent of crystallisation) resolidifying and again melting at 165.5–165.7°. Paperchromatographic tests employing sodium borate impregnated paper and butanol, ethanol, water (5:1:4) or benzene, ligroin (b. p. 80–120°) as developers indicated the absence of carvacrol in the mother liquor. There was an extremely weak spot corresponding to α -thujaplicin.

2. *Extraction with ligroin.* The ground wood (100 g) was extracted continuously with hot ligroin for 15 hours. The extract (2.3 g) was an oil which easily crystallised. By dissolution in dilute potassium hydroxide solution and precipitation with hydrochloric acid a yield of 1.6 g of practically pure β -thujaplicin was obtained.

3. *Extraction with alkali.* The ground wood (100 g) was mixed with a 2 % solution of potassium hydroxide (500 ml). After fifteen minutes the mixture was filtered and this operation repeated twice. The combined extracts were acidified with hydrochloric acid and shaken with ether. In this manner a fraction insoluble in ether (4 g) and a fraction soluble in ether were obtained. The latter was distilled *in vacuo* (10 mm) yielding a volatile product (2.5 g) which crystallised directly and from which pure β -thujaplicin (2.1 g) was isolated.

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The Diastereomers of α -Methyl- α' -ethyl-glutaric Acid

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In connection with an investigation into configurative relations in progress at this institute Schotte¹ has studied the infrared absorption spectra of the two isomers of α -methyl- α' -ethyl-glutaric acid. As early as 1946 these isomers were prepared by the author and this communication describes the method used.

The separation of the two isomers was performed by making use of the different solubility of their acid calcium salts and after several recrystallisations from water they melted at 83.5–84.5° and 105.5°, respectively. According to Schotte¹ the configuration of the low melting acid is probably mesoid and that of the high melting racemoid. On mixing the two isomers in about equal quantities, the mixed melting point was 62.5–64°. Owing to shortage in material only a few mixed melting points could be obtained but these suggest an eutectic at about 62° with approximately 40 % high melting acid.

Another method of separation has been used by previous authors²⁻⁴, viz. by converting the mixture of diastereomeric α -methyl- α' -ethyl-glutaric acids to the imides which are then separated and hydrolysed. The high melting acid thus prepared was reported² to melt at 107°, the low melting product must, however, still have been a