The Chemistry of the Natural Order Cupressales. XV.* Heartwood Constituents of *Austrococeras chilensis* (D.Don), Florin et Boutelje (= *Libocedrus chilensis* (D.Don)Endl.)

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Most of the genera of the family Cupressaceae belong either to the northern or to the southern hemisphere but one; *Libocedrus sempervirens* 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*, *Austrococeras*, *Pseudococeras* and *Libocedrus sempervirens* (all southern hemisphere).

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 (*L. a. str.*), New Zealand, which is in agreement with unpublished results from this laboratory.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 also of the Cupressaceae — B. Thomas, unpublished).

Zavarin and Anderson‡ found in the Californian *Heyderia decurrens* (Torr.) K. Koch (*Libocedrus decurrens* Torr.) carvacrol, hydrothymoquinone, thymoquinone, the two hydrothymoquinone monomethyl ethers, libocedrol (which is a dehydrogenation product of one of them) and (Dr. Anderson, private communication) β-thujaplicin. *Heyderia*, therefore shows certain chemical affinities to the northern Tetraclinias from which Grimal§ isolated the three first mentioned compounds but which, generally, has been regarded to be related to a southern tribe of the Cupressaceae. The East Asian *Heyderia formosana* (Florin) Li (= *Libocedrus formosana* Florin) which was studied some time ago by Ishikawa§, apparently, differs considerably from *H. decurrens* containing mainly a series of highly interesting terpenoid acids among which shononic acid is the best known. The presence of unidentified “phenols” was also reported.

We have now examined the heartwood of *Austrococeras chilensis* (D. Don) Florin et Boutelje (*Libocedrus chilensis* D. Don) which is endemic to Chile and constitutes the sole recent species of the genus *Austrococeras*. Taxifolin and β-thujaplicin were isolated. It is the first instance of a tropoloniiferous member of the family Cupressaceae occurring in the southern hemisphere. The yield of β-thujaplicin was unexpectedly 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 “phenol coefficient” of β-thujaplicin‡ is over 100, the wood is extremely durable and resistant to the attack of wood destroying fungi (Docent E. Rennerfelt, private communication).

Experimental. 1. Extraction with acetone. The powdered heartwood (1240 g) was extracted 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 shaken 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 (1.2 g) crystallised. Solution A was evaporated to dryness and the residue boiled with ligroin (b. p. 90—120°) (3 x 500 ml) when 38 g material passed into solution (“B”) leaving an insoluble residue (41 g) which was worked up like A employing, however, 30 ml of chloroform. 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 recrystallisation from water, m. p. 238—239°, (not depressed on admixture with an authentic specimen), [α]D 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 paper chromatography em-

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ploying 1) neutral paper, 2) boracic acid improregnated paper, and as developers 1) hypophase of chloroform, ethanol, water (8:2:1) and 2) ethylphase of benzene, ethanol and boracic acid saturated water (6:2:1). Only a single spot corresponding to that of taxifolin was observed on spraying with bidiazotised 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 (300 ml), a 10% sodium carbonate solution (4 x 300 ml) and a 5% potassium hydroxide solution (3 x 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 “alkalin fraction” (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 185.5-185.7°. Paper chromatographic 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 a-thujaplicin.

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 Schotte2 the configuration of the low melting acid is probably meso 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 authors3, 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 reported4 to melt at 107°, the low melting product must, however, still have been a