A REVIEW OF YELLOW CEDAR (*CHAMAECYPARIS NOOTKATENSIS* [D. DON] SPACH) EXTRACTIVES AND THEIR IMPORTANCE TO UTILIZATION

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ABSTRACT

The major foliage and wood extractives, such as terpenes, sesquiterpenes and tropolones, from yellow cedar (*Chamaecyparis nootkatensis*) are reviewed and their properties are discussed in relation to color, durability, distinctive odor, and stain susceptibility.

Keywords: *Chamaecyparis nootkatensis*, extractives, foliage, color, odor, durability, stain, review, chemical structure.

INTRODUCTION

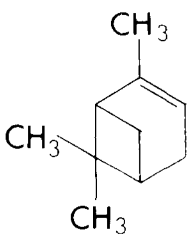
The structural constituents of coniferous wood substance, namely holocellulose and lignin, are similar in chemical composition and amount whether they are isolated from Douglas-fir (*Pseudotsuga menziesii*) or yellow cedar (*Chamaecyparis nootkatensis*). The marked chemical differences in properties among most conifers, in fact, are due to the nature and quantity of the ether, alcohol-benzene, and hot-water soluble components called extractives. This can readily be seen from Table 1, which is a composite of data obtained from several sources (Barton and MacDonald 1971; Fengel and Grosser 1975; Kurth 1950; Browning 1963). Just as in the case of western red cedar (Barton and MacDonald 1971), yellow cedar owes its color, distinctive odor and durability to its characteristic extractives which, although present in lesser amount, are unique chemical substances with very interesting properties. This paper is the first review of yellow cedar extractives to relate their chemistry with the utilization of the species.

CHEMISTRY OF YELLOW CEDAR FOLIAGE EXTRACT

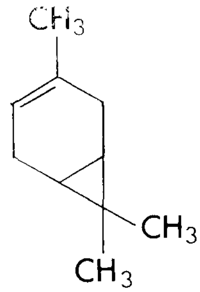
The first recorded investigation of yellow cedar foliage occurred in 1926 (Clark and Lucas 1926). Although these workers isolated both the wood and leaf oils, they confined their detailed study to the latter, identifying α-pinene and limonene and obtaining evidence of β-pinene, sabinene, and ρ-cymene.

The most definitive study, however, must be credited to Cheng and von Rudloff, who in 1970 used the modern technique of gas-liquid chromatography to separate and analyze the volatile leaf oil (Cheng and von Rudloff 1970a, b). They showed (−)-α-pinene (1), (+)-3-carene (2), and (+)-limonene (3) to be the main constituents. In addition, nine monoterpene hydrocarbons, seven oxygenated monoterpenes, six sesquiterpene hydrocarbons, nerolidol, cedrol, bisabolol, α-cadinol, nine diterpene hydrocarbons (including one new one previously unidentified), manoyl-,13 and 8-epimanoyl- and 8,13-diepimanoyl oxides, phyllocladol, six n-alkanes, three alkanals and nine C_5-branched-chain or aromatic esters of isovaleric, 3 methyl-2 and 3 methyl-3 butenoic acids were identified.

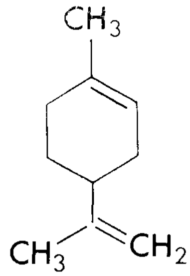
This rather complex mixture of minor components is invaluable in studying tree-to-tree variability, as well as in deciding species changes through chemotaxonomy. This latter issue was thoroughly discussed in a review by Erdtman and Norin, particularly with respect to the possibility that yellow cedar should be included with *Chamaecyparis henryae*, a species growing in the southeastern United States (Erdtman and Norin 1966). It was concluded



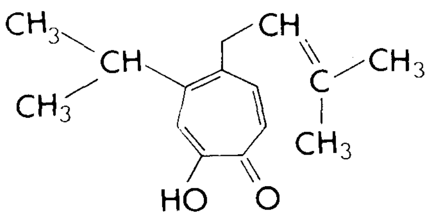
1 PINENE



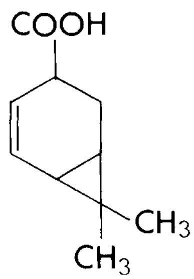
2 3-CARENE



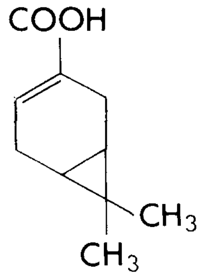
3 LIMONENE



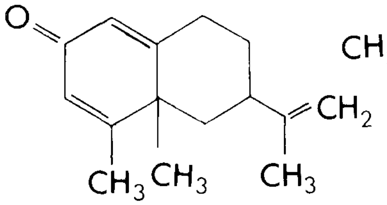
4 NOOTKATIN

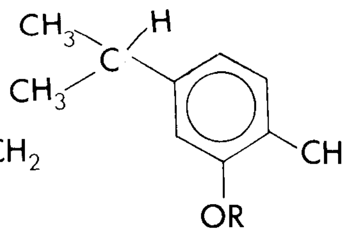


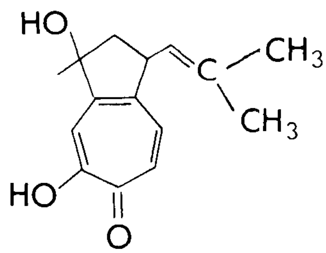
6 CHAMIC ACID



7 CHAMINIC ACID







5 R=H, CARVACROL

9 NOOTKATONE **8** R=CH3, METHYL CARVACROL **10** CHANOOTIN

Major constituents in yellow cedar leaf and wood extracts.

TABLE 1. *Structural Extractives of Four British Columbia Conifers*

Species	Holocellulose[a] %	Lignin[a] %	Ash[a] %	Solubility[b] in %			
				Alcohol-benzene	Ethyl ether	1% NaOH	Hot water
Douglas-fir (*Pseudotsuga menziesii*)	71.3	28.4	0.3	1.6- 5.5	1.2-1.3	13.7	2.8- 6.5
Western hemlock (*Tsuga heterophylla*)	67.1	30.4	0.5	1.6- 5.8	0.3-1.3	11.7	2.3- 5.3
Western red cedar (*Thuja plicata*)	67.3	32.5	0.3	8.2-13.8	0.7-3.2	21.0	7.3-11.0
Yellow cedar (*Chamaecyparis nootkatensis*)	69.9	30.0	0.2	-	1.0-2.5	13.4	2.1- 2.9

[a]Holocellulose, lignin and ash figures are on a moisture-free, extractive-free basis.

[b]Solubility figures are on a moisture-free basis.

that there was insufficient chemical evidence at that time to justify the reclassification of yellow cedar. In 1970, Anderson and Syrdal reported on the stereochemistry of the sequiterpene leaf fraction and discussed the biogenetic importance of these stereo assignments (Anderson and Syrdal 1970a).

CHEMISTRY OF YELLOW CEDAR WOOD EXTRACT

Although Clark and Lucas had done a preliminary investigation of the steam distillate of yellow cedar wood when they examined the foliage, it remained for Carlsson et al. to study this aspect of yellow cedar chemistry in depth (Carlsson et al. 1952). They steam distilled finely divided heartwood and obtained two main fractions. The first was a pale yellow oil, which was followed by further material that distilled more slowly and crystallized out in the form of colorless plates upon cooling the distillate. This crystalline material was further purified and shown to be a hitherto unknown tropolone for which they proposed the name nootkatin (4). The structure of nootkatin was fully characterized by Duff and Erdtman using classical chemical methods, together with an X-ray analysis of its copper complex (Duff and Erdtman (1954). It should be noted that the earlier work of Clark and Lucas failed to yield crystals of nootkatin, since it reacted with their iron condenser to give the deep red iron-tropolone chelate.

Recently gas-liquid chromatography (Johnson and Cserjesi 1975) has been used to separate nootkatin from other tropolones. Further fractionation of the oil into acidic and neutral fractions yielded carvacrol (5) and two new acids, chamic (6) and chaminic (7), in the acidic fraction and unknown compounds in the neutral fraction (Erdtman et al. 1956). The absolute configurations of these acids were reported by Norin (Norin 1964). Subsequent work of Erdtman and Hirose investigated this neutral fraction and discovered methyl carvacrol (8) and a new sequiterpene ketone they named nootkatone (9) (Erdtman and Hirose 1962). Two years later, Norin reinvestigated the acidic fraction and discovered a bicyclic C_{15}-tropolone he named chanootin (10) (Norin 1964). Other nootkatane sesquiterpenes, valencene and nootkatene, found in the heartwood are described (Erdtman and Topliss 1957, Anderson and Syrdal 1970b).

CONTRIBUTIONS OF YELLOW CEDAR EXTRACTIVES TO THE PROPERTIES OF WOOD

Clearly the most important contribution of yellow cedar extractives is that they are solely responsible for the excellent durability of the wood. Rennerfelt and Nacht found that nootkatin, chamic acid, and even the neutral fraction possessed fungicidal activity (Rennerfelt and Nacht 1955). They reported that nootkatin inhibited fungus growth at 0.001 to 0.002 percent concentration, while chamic acid inhibited fungi at 0.01 to 0.02 percent. Erdtman confirmed the toxicity of nootkatin and chamic acid and included chaminic acid also as being fungicidal (Erdtmann 1955). Finally, even carvacrol was shown by Anderson to have fungicidal properties (Anderson 1961). Thus, it would seem that nearly all the isolated yellow cedar extractives and in particular the tropolones, which compare in toxicity with pentachlorophenol, contribute to yellow cedar's high durability. Investigations of fungal-induced chemical changes in yellow cedar have also been reported (Smith and Cserjesi 1970, Cserjesi and Smith 1968).

Another important property of yellow cedar, namely insect resistance, has been attributed to its extractives by both Carlsson et al. and Erdtman (Carlsson et al. 1952; Erdtman 1952). Although no experimental evidence was given, the recent discovery by Barton et al. that thujic acid from western red cedar is an effective juvenile insect hormone (Barton et al. 1972) lends credence to the possibility that chamic or chaminic acid in yellow cedar may show similar activity.

Finally, yellow cedar extractives are important in explaining stains on the wood and difficulties in painting and varnishing yellow cedar lumber. As previously mentioned, yellow cedar heartwood contains tropolones that will easily react with trace amounts of iron to give pink stains or, with larger amounts of iron, to give brown stains. In the presence of moisture, iron will also react with other heartwood phenolic extractives to give black stains. It follows, therefore, that all contact with iron should be avoided. Aluminum and properly galvanized iron nails and fasteners are acceptable. Copper and brass will react with the tropolones in the wood to give green chelate stains, which could be objectionable under certain conditions.

Although the combined ether and water soluble extractive contents of yellow cedar range from 3.1 to 5.4, unlike other common western conifers (Table 1), the ether solubles (range 1.0 to 2.5) represent nearly half the combined total. These ether solubles consist of the oily extractives already discussed and tend to interfere with the absorption of oil-based paints and varnishes causing uneven coating and slow drying. Removal of the more volatile oil by kiln drying, by extensive air seasoning, by solvent treatment, or by sealing the surface with diluted varnish is considered necessary for satisfactory results.

While this review has been restricted to yellow cedar, tropolones of one type or another are found in four other species of the genus *Chamaecyparis*, namely *lawsoniana*, *tyoides*, *formosensis* and *taiwanensis* (Zavarin et al. 1959). Thus, depending on the amounts present, the tropolone-related properties of staining and durability described for yellow cedar would apply to these species also.

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