

# PRODUCTION OF THE 4-THUJANOL FLAVORING AGENT IN CRYSTAL FORM

Producing pure and natural (E)-(R)-4-thujanol in abundance with a competitive price is likely to boost the use of 4-thujanol.

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*The food industry uses a few essential oils, such as marjoram and thyme, containing a small percentage of 4-thujanol.*

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**E**)-(R)-4-Thujanol (also known as *trans*-4-thujanol or *trans*-4-sabinene hydrate, as seen in F-1A) is a flavoring substance with a delicious taste of fresh minted thyme. The food industry uses a few essential oils, such as marjoram and thyme, containing a small percentage of 4-thujanol (a mix of *cis* and *trans* isomers). However, due to its absence in the catalogues of aromatic suppliers, less than 100 kg of pure and natural 4-thujanol equivalent are traded worldwide every year.<sup>1</sup> This is very small in comparison to other aromatic substances (several tons per year).<sup>2</sup> Synthetic analogue<sup>a</sup> can be supplied with a pricey value of \$44.00 per gram for a 90% pure package.<sup>3,4</sup>

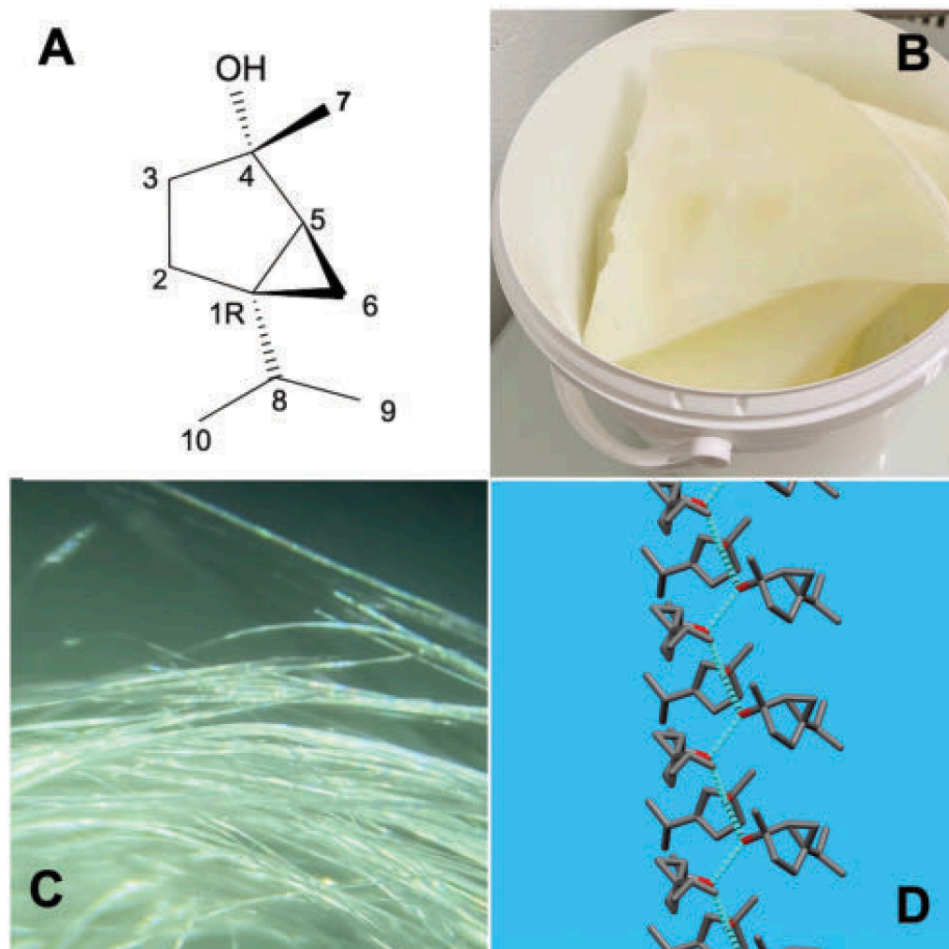
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Therefore, producing pure and natural (E)-(R)-4-thujanol in abundance with a competitive price is likely to boost the use of 4-thujanol.

Our laboratory and partners have recently published an innovative way to produce (E)-(R)-4-thujanol from a selected ecotype of thyme from the garrigue of Provence.<sup>5</sup> The extraction was done using traditional steam distillation. Usually, such a process results in an aromatic liquid (an essential oil). Because of the physical and chemical properties of (E)-(R)-4-thujanol, we observed a liquid to solid phase transition and accumulation of raw crystals, mainly made of (E)-(R)-4-thujanol (up to 80%). The first trial in the field yielded several kilograms of this raw crystal (F-1B).

From the raw crystal, an additional step of purification involving a sublimation/condensation cycle produced an almost pure crystal of

- F-1** **A.** (E)-(R)-4-thujanol. **B.** Raw crystal of (E)-(R)-4-thujanol. **C.** Crystal fibers of (E)-(R)-4-thujanol. **D.** Molecular structure of crystalline edifice. Superposition of trimers in helix structure. Red: alcohol. Cyan: hydrogen bond. Grey: carbon skeleton.



(E)-(R)-4-thujanol (>95%), which looks like translucent fibers (F-1C).

This crystalline structure is remarkable because it was unexpected that the (E)-(R)-4-thujanol, with such a simple structure, could build crystalline fibers. Specifically, (E)-(R)-4-thujanol forms a trimmer that overlays itself indefinitely at a slight angle, constituting a chiral P-type helix (F-1D). At the heart of the structure, the alcohol functions are interconnected through hydrogen bonds.

It is worth noting that the entire extraction and purification process is solvent-free, and therefore environmentally friendly. A part of this production is already labeled by Ecocert (EU organic agriculture).

Such a high purity of (E)-(R)-4-thujanol already has the interest of a French Michelin-starred chef, Claude-Emmanuel Robin, who is working on the development of new products with new flavors.

In addition to the usual benefits of a near-pure natural aroma for perfumers and flavorist, the fibrous structure of the crystal opens up new possibilities, such as the manufacture of bioactive fibrous assemblies.

(E)-(R)-4-Thujanol is also a molecule of known physiological properties: pollen attractor (activator of bee antennae) and insect repellent (female bark beetles).<sup>6,7</sup> The production of pure and natural (E)-(R)-4-thujanol in abundance is likely to stimulate research on its physiological functions and to support applications in nature or culture.

(E)-(R)-4-Thujanol is quite an inert molecule (except in extreme pH). (E)-(R)-4-Thujanol does not carry unsaturation that may be responsible for the formation of hydroperoxide. This means that it cannot be altered by the presence of molecular

oxygen. The alcohol function, carried by tertiary carbon, cannot be oxidized. All this is a precious asset for its use, the maintenance of its active properties over time and for its storage. The pure (E)-(R)-4-thujanol crystal has a melting point of 60 °C so it can be sent for several days' travel without being modified.

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