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Vanillin, Cis-Terpin Hydrate, and Cis-Terpin as Ice Nucleators

Abstract. *Vanillin,* cis-*terpin hydrate, and* cis-*terpin cause ice nucleation at relatively high threshold temperatures. Trace quantities of these substances should exist in the natural atmosphere and may act as ice nuclei.*

Many organic crystalline substances can nucleate ice formation in supercooled water (*1*), and some act at relatively high threshold temperatures, for example, α-phenazine at −3.5°C, *l*-leucine at −4.5°C.

We have tested, for nucleating activity, a number of crystalline organic compounds which occur among essential oil substances. Testing was done in a 110-liter cold box. Small crystals of the test substances were allowed to settle onto a supercooled soap film suspended in the box. Any ice nucleation produced is readily observed from the rapid formation and growth of ice crystals in the film (*2*).

Vanillin crystals (recrystallized from water) act as ice nuclei on the soap film at a threshold of −4.5°C; when obtained by recrystallization from ethyl alcohol, the ice nucleation temperature is reduced to −6°C. Sublimed vanillin crystals act at −9°C. It is interesting that vanillin is produced photochemically by the action of ultraviolet light on vapors of isoeugenol, presumably through oxidation of the isoeugenol by ozone produced by the radiation (*3*).

Terpin hydrate shows a threshold temperature of action of −3.5°C on a soap-film detector. However, crystals supported on a glass slide in the cold chamber show no overgrowth of ice crystals above −6°C, and they act at this temperature only when exposed in a cloud of supercooled droplets.

When terpin hydrate is heated it loses water at 100°C and sublimes. The sublimed crystals have a melting point of 103°C and are presumably anhydrous *cis*-terpin. We find that sublimed terpin crystals nucleate a soap film at −2.5°C. Since *cis*-terpin readily absorbs water to re-form terpin hydrate, it is an interesting point whether the sublimed crystals act in the anhydrous form or as the hydrate to freeze the water.

The following substances were found to be inactive above −11°C: thymol, benzyl cinnamate, cinnamic alcohol, and terpineol.

Went (*4*) has estimated the mass of essential oils released annually by the biosphere to the atmosphere at 1.5×10^{11} kg. Two of the most widely distributed substances among the essential oils are the terpenes dipentene (*dl*-limonene) and α-pinene (*5*). Dilute mineral acids readily convert these substances into terpineols, terpinolene, terpin hydrate, cineole, and a number of other substances, depending on the exact conditions of the reaction, such as temperature, acidity, agitation, and others (*5*).

The oxidation of SO_2, a constituent of the natural atmosphere, to SO_3 can proceed either photochemically (*6*) or in solution in cloud droplets (*7*). The bulk of the resulting H_2SO_4 is apparently neutralized rather quickly by traces of atmospheric ammonia. However, the *p*H of rain water is 4 to 6 (*8*), and cloud droplets may likewise be assumed to be acidic. When cloud droplets evaporate the *p*H will fall sharply, so that in theory trace quantities of crystalline reaction products could be formed from pinene, dipentene, and other plant vapors adsorbed onto acidic cloud droplets and condensation nuclei in the atmosphere.

We have exposed drops of 10 and 25 percent H_2SO_4 to saturated atmospheres of both pinene and dipentene at room temperature and at −5°C. Very small quantities of crystalline reaction products are quite readily produced, but we have not positively identified them.

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