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Naturally Occurring Persistent Organic Pollutant

by Ryan Woitas

(Chemistry 1552)

Native across forests of Central and Northern Europe lives a species so vulgar, it would be hard pressed to think that such a beast could possess a certain quality that gives significant meaning to its existence. With its compact body, stubby legs, and wide head, the bristly haired wild boar may provide insight to chemists about an organic compound called drosophilin A (p-methoxytetrachlorophenol) that closely resembles persistent organic pollutants. Industrial persistent organic pollutants are halogenated molecules that are intrinsic with environmental toxicity.¹ First studied by chemists in 1952, drosophilin A has become part of the modern scientific community due to an alarming discovery of the potentially fatal organic compound residing in wild boar meat sold in German food markets.

Persistent organic pollutants (POPs) are not uncommon; there are theoretically reported 209 polychlorinated biphenyls (POPs) that differ from each other only by their constituents quantities, primarily the chlorine, and substitution positions. POPs are known for their hydrophobic and lipophilic desires as well as displaying attractive tendencies towards organic solids when in aqueous environments in an effort to avoid the liquid phase. What makes POPs especially harmful to mammalian body systems is the attractive nature of the toxic molecules to lipid storages, which consequently causes the chemical to remain in mammalian adipose tissue storages, indefinitely. POPs also have an affinity for traveling; POPs may enter the gas phase in certain environmental conditions, as temperatures warm, POPs are expelled into the lower atmosphere where they can travel long distances due to their resilient nature to breaking down or forming more stable compounds in the air. Such a characteristic of POPs is a cause of concern since it is possible for the toxic compounds to travel far from their origin, depositing into river beds contaminating water and aquatic life.²

Drosophilin A was the first natural chlorinated compound studied and analyzed to contain a halogenated benzene ring that was first isolated in 1952 from a basidiomycete, a fungus whose spores develop in basidia.³ Basidiomycetes are the parent group of most familiar mushrooms and toadstools. Table 1 displays the minimum various species that are known to contain drosophilin A. Significance of the aforementioned discovery answers questions that arose to a group of scientists in Germany, who made an astonishing discovery while performing a routine safety inspection of a food market, specifically in the markets supply of wild boar meat. Routinely analyzed samples of wild boar meat tested positive for drosophilin A, however, since these animals are usually hunted in heavily wooded areas away from industrialization (the primary source of POPs) it became apparent that the source of drosophilin A contained within the wild boar meat was from something benign: a subspecies of basidiomycete known to be a part of the wild beasts diet.

¹ de Jong, Ed et al. "Significant biogenesis of chlorinated aromatics by fungi in natural environments." *Applied and environmental microbiology* 60.1 (1994): 264-270.

² Jones, Kevin C, and P De Voogt. "Persistent organic pollutants (POPs): state of the science." *Environmental Pollution* 100.1 (1999): 209-221.

³ Anchel M. 1952. Identification of drosophilin A as p-methoxytetrachlorophenol. *J. Am. Chem. Soc.* 74:2943.

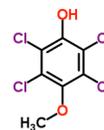


TABLE 1 DROSOPHILIN PRODUCTION BY BASIDIOMYCETES

Organism	Drosophilin A (mg/L)
<i>Agaricus arvensis</i>	0.500 ⁴
<i>Bjerkandera adusta</i>	0.500 ⁴
<i>Coprinus plicatilis</i>	20.0 ⁵
<i>Peniophora pseudeopini</i>	1.00 ⁴
<i>Phellinus fastuosus</i>	15.7 ^{4&6}
<i>Psathyrella subatrata</i>	3.20 ⁷

The significance of the German scientists' discovery centers on the fact that most knowledge of POPs' environmental impacts deal primarily with amphibious habitats; scientists hope to shed light on the continental behavior of POPs through further analysis of the samples of drosophilin A collected from the market boar meat. The team of German Scientists proliferating the investigation of wild boar meat contamination is being led by Walter Vetter and his technical assistant Katja Lehnert at the University of Hohenheim, one of Germany's top-tier universities. Analytical techniques used by Vetter and his team are known for producing incredibly accurate results: gas chromatography and mass spectrometry, which helped the scientists confirm that the potentially toxic compound collected from the German markets boar meat was indeed drosophilin A. Although Vetter and his colleagues cannot pinpoint the exact species of basidiomycete ingested by the wild boar, Vetter is certain that the boar acquired drosophilin A from consuming mushrooms as long term data suggest, based on the fact that there are numerous mushroom species that can house the chemical organic compound that are known to be consumed by wild boar.

Drosophilin A closely resembles a POP, known toxic industrial chemicals. What Walter Vetter hopes to achieve is an understanding of the effects of drosophilin A on humans, because an apparent risk will initiate recourse to prevent harm to individuals that consume wild boar meat even if it's (consumed) sparingly, since the intrinsic ability of POPs to remain in adipose storages. However, Vetter and his team are hoping to discover that the wild boar has developed a defense against the compounds undesirable effects along with coming up with an answer to the question, why do species of basidiomycetes contain the toxic compound in the first place? Chemist Gordon W. Gribble of Dartmouth College stated, "If the compound (drosophilin A) turns out to be nontoxic to

⁴ Teunissen PJM, Swarts HJ, Field JA. 1997. Screening of ligninolytic basidiomycetes for the production of Drosophilin A (tetrachloro-4-methoxyphenol) and Drosophilin A methyl ether (tetrachloro-1,4-dimethoxybenzene). *Appl. Microbiol. Biotechnol.* In press.

⁵ Bastian W. 1985. *Vergleichende Untersuchungen zum Sekundärstoffwechsel an Coprophilen und Erdoder Holzbewohnende Basidiomyceten*. PhD thesis. Univ. Kaiserslautern, Germany (In German).

⁶ Singh P, Rangaswami S. 1966. Occurrence of O-methyl-drosophilin A in *Fomes fastuosus* Lev. *Tetrahedron Lett.* 11:1229–31.

⁷ Kavanagh F, Hervey A, Robbins WJ. 1952. Antibiotic substances from basidiomycetes. IX. *Drosophila subatrata* (Batsch:Fr) Quel. *Proc. Natl. Acad. Sci. USA* 38:555–60.

the boars, it could provide useful lessons about how to construct halogenated compounds so they don't end up becoming a health or environmental threat.”

July 15, 1952, proceedings of the National Academy of Sciences published research on four variations of drosophilin A pertaining to the possible antibiotic properties of the aforementioned substances found in twelve species of basidiomycetes from nine genera; the following information gives modern chemists an advantage in terms of analyzing the POP analogue. Antibacterial activity was measured against seven bacteria and data showed that drosophilin A was active primarily against only staphylophage, particularly against strains of staphylococci and *B subtilis*. However, the fact remains that the inevitable production of naturally occurring drosophilin A remains as an environmental significance.⁸

The National Academy of Sciences were also able to deduce information during their experimentation in 1952 about the chemical structure and properties of drosophilin A. Experimentation was performed by analyzing a crystalline variant of the organic compound after firstly purified with a benzene solution and treatment with decolorizing carbon. Drosophilin A was determined to have: a melting point of 118 °C; solubility in hexane, benzene, acetone, alcohol, chloroform, ether and slightly soluble in water; and drosophilin A was unable to be extracted by concentrated hydrochloric acid, which suggests that the organic compound lacks alkaline properties, however the chemical is only slightly acidic since it was unaffected by attempts to extract appreciable amounts with a chloroform solution containing bicarbonate. Chemists of the National Academy of Sciences were able to determine the molar mass of drosophilin A cryoscopically in exaltone. Drosophilin A was determined to have the empirical formula of $C_{13}H_9O_4Cl_7$.⁹

The fact remains that continued research surrounding drosophilin A and other drosophilins is currently underway due to findings of the potentially fatal organic compound in food consumed by human beings. Rigorous standards set by Germany surrounding testing for food contaminants has proven to be effective, since it is still not known pertaining to the lethality of drosophilin A to humans and mammals alike. Close resemblance of drosophilin A to POPs is enough motivation for chemists to continue researching the less than well-known compound, as to prevent possible future catastrophic events from occurring regarding potential toxicity of drosophilin A in human populations.

⁸ de Jong, Ed et al. “Significant biogenesis of chlorinated aromatics by fungi in natural environments.” *Applied and environmental microbiology* 60.1 (1994): 264-270.

⁹ The quantitative analyses and molecular weight determinations were made by the Huffman Microanalytical Laboratories, Denver, Colo..