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Supernatural Products: An Illiterature Review

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Abstract: Supernatural products are just like any other molecules, only more so. This illiterature review presents a recap of supernatural products with structures that have been elucidated or reassigned in the last decade(ish).

Introduction

It is often stated that nature is the ultimate chemist. Chemists have marvelled at the elegance, intricacy, and complexity of natural products since the means of structural determination first became available. For some chemists, that fixation has spilled over into fetishism. Why else would there be so many total syntheses of morphine when poppies make it by the tonne? Why else would someone spend years conducting a 40-step synthesis of tetrodotoxin on a microgram scale, when the only reason it doesn't kill you is that you couldn't make enough of it? This review is targeted at those people.

Supernatural products represent a subclass of biomolecules, defined by fiendish substitution patterns, hypervalency, intricate ring systems, unconventional functional groups and tortuous bond angles.¹ The pharmacological activity of such compounds is typically commensurate with their structural complexity, and with the difficulty of their synthesis, which is a right pain in the hole. In these times of superbacteria, antibiotic resistance and flesh-eating fungi,² chemists are increasingly turning to supernatural products in a last-ditch attempt to prevent the collapse of human civilisation. This review presents the progress in the field of supernatural products made in the last decade.³ The molecules discussed herein are divided into 1) recent discoveries, 2) structural reassignments and 3) tentative or conjectural structures, in lieu of definitive characterisation by X-ray crystallography.⁴

Recent Discoveries

Monoalzeamine D (1)

Isolated from a Venetian sea-sponge (*Gioconda vinchianes*), Monoalzeamine D is truly perplexing compound.⁵ It acts as an attractant to fish, which have been observed to gather in great

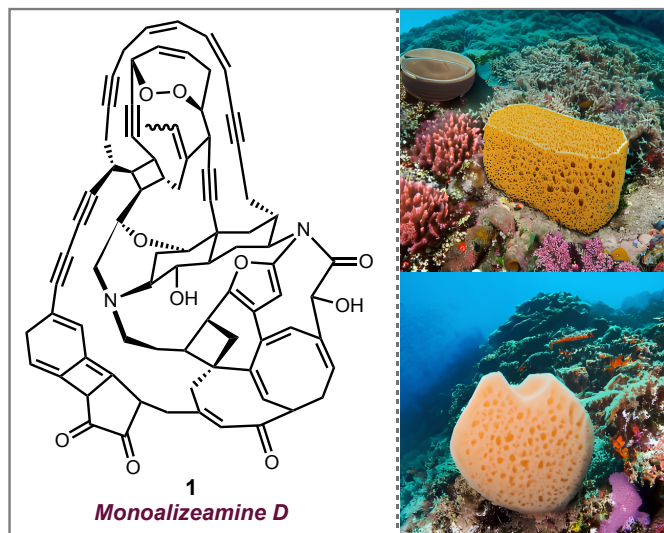


Figure 1: Monoalzeamine D and the sponge (*G. vinchianes*) from which it is obtained. Image credit: Craiyon.com.

numbers around *G. vinchianes* colonies, but the benefit obtain by the sponge from this behaviour is unclear. In humans, Monoalzeamine D provokes a wide range of symptoms. Some test subjects report experiencing euphoria, awe, and wonder, while others experienced a slight lachrymatory effect. Around 30% of those exposed reported no symptoms at all. The structure of Monoalzeamine D has captivated chemists since it's discovery. The configuration of the alkene at C15 is enigmatic, with no clear consensus on an *E* or *Z* orientation of the methyl group. It is, however, widely accepted that the peroxide does seem to follow you around the room.

Tutankhamine (2)

In the gold mines of the eastern Egyptian desert, the intrepid explorer can find one of nature's purist beauties. The golden scarab beetle (*Chrysina auriphila*) is resplendent in its gilded carapace, and is believed to have inspired J.B.S. Haldane to opine "if there is a God, he must be inordinately fond of beetles." If one takes several kilos of these magnificent creatures, macerates them in blender and carefully extracts the

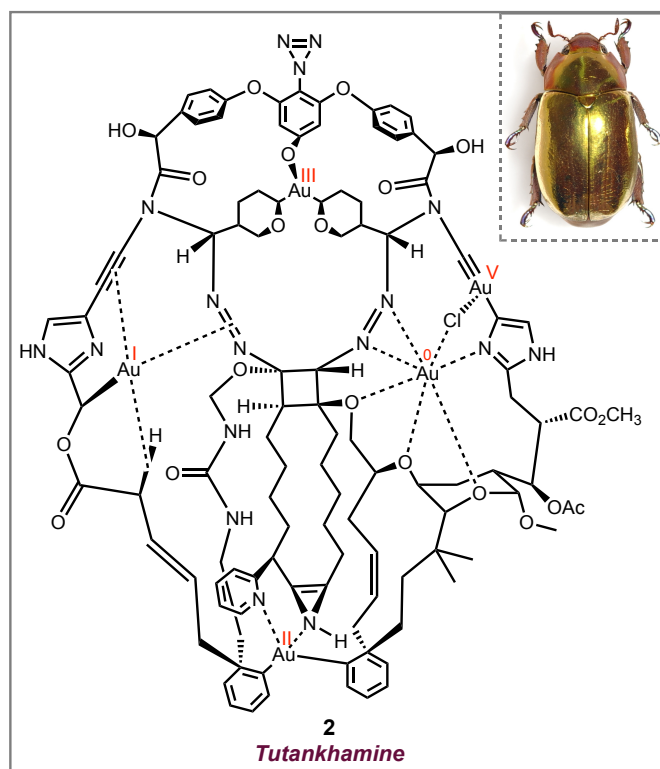


Figure 2: Tutankhamine and (inset) the golden scarab beetle, *C. auriphila*.

Inset image credit: Musée d'histoire naturelle de Lille (https://commons.wikimedia.org/wiki/File:Chrysina_aurigans_GLAM_muséum_Lille_2016.jpg), <https://creativecommons.org/licenses/by-sa/4.0/legalcode>

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pulp with MeCN, it is possible to obtain something even more beautiful.⁶ Tutankhamine is that most elusive of treasures: a gold complex that is useful for something. Specifically, its useful for killing the kind of things that eat scarab beetles. Its toxicity extends beyond slaying the odd lizard though; entomologists have theorised that this devilish toxin is behind the “curse of the pharaohs” and is responsible for the death of Lord Carnarvon among others. This may be true, or it may be because these are entomologists, and their answer to any question is “beetles”. Aside from its questionable history, tutankhamine is also notable for containing five gold atoms in five different oxidation states and two pentavalent carbons, which is probably why no synthesis has been reported to date.

Mobiustrine A (3)

The polyketide Mobiustrine A was obtained from that perpetual font of novel chemistry: a solvent waste container.⁷ Or, more specifically, a mould growing beneath such a container: *Kleptomycetes negligencii*. When organisms inhabit environments as inimical to life as fume hoods, they often develop novel biochemistry to help them survive (e.g., *Taq* polymerase). Indeed, it is speculated that Mobiustrine A is an enzymatic cofactor for the conversion of dichloromethane to CO₂ in a novel form of cellular respiration. Mobiustrine A shows some early promise as an antimutagenic agent, but research on the subject has been impeded because the substrate keeps killing the researchers.

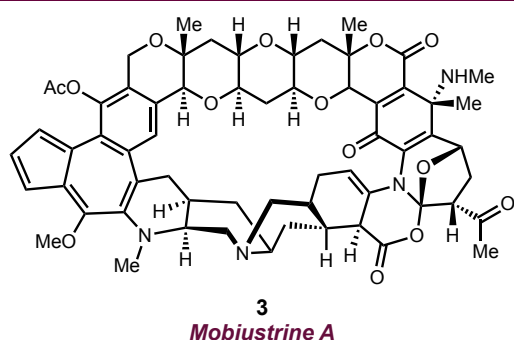


Figure 3: It's Mobin time.

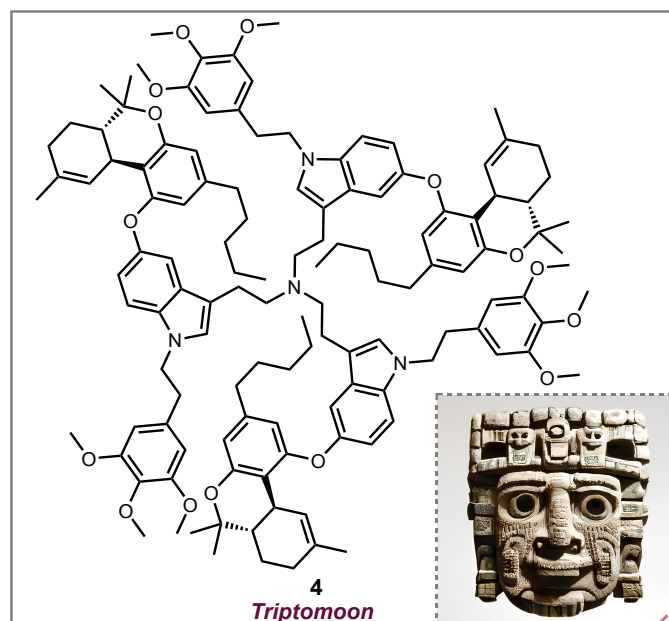


Figure 4: The structure of the psychedelic alkaloid Triptoomon. Inset: A 9th century Mayan carving of Emperor Pánámácánál, featuring the harrowed gaze of a triptoomon addict. Inset image credit: Craiyon.com.

(+)-Triptoomon (4)

(+)-Triptoomon is a potent psychedelic alkaloid isolated from a Mesoamerican cactus, *Lophophora spectacula*. It was used extensively by the first civilisations of the Americas as a means of contacting the gods, divining the future and enlivening dinner parties, but it was only isolated in pure form in 2019.⁸ According to legend, this substance was responsible for the 9th century collapse of Mayan society, when Emperor Pánámácánál smoked the cactus and launched an invasion of the sky (Fig. 4).

Kajulamine B (5)

Kajulamine B is an enzymatic cofactor found in the Japanese giant salamander *Andrias godzilla*.⁹ The favoured theory pertaining to its role in the salamander's biology is that Kajulamine acts as a growth factor and as an electron-shuttle for cellular respiration. It is remarkable for bearing a coordinated uranyl hydroxide in the unusual +2½ oxidation state. As such, it is anticipated to display fascinating redox properties, but studies of this area to date have been hampered by a lack of material. Kajulamine B has an extremely low tissue concentration, which necessitates dissolving several salamanders in boiling DMSO to obtain a usable sample mass. As such, a synthesis of Kajulamine B is highly desirable.

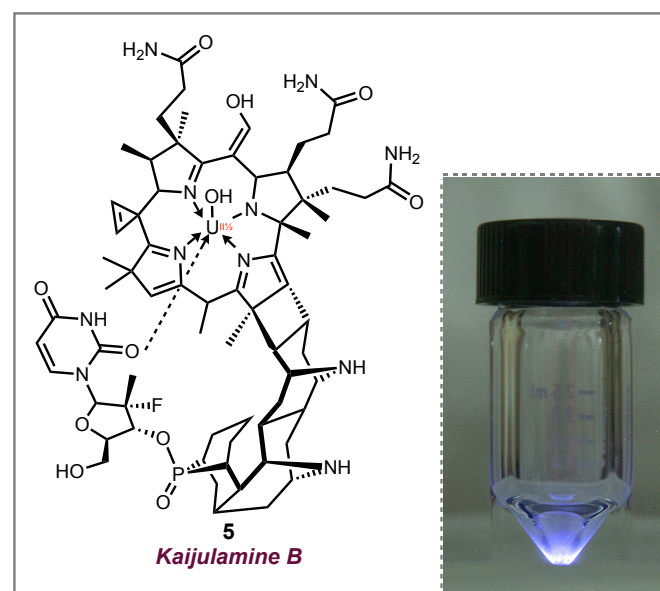


Figure 5: Samples of kajulamine are luminous, not due to radioactivity, but to rapid disproportion to U(II) and U(III).

Inset image credit: Dr Andrew R. Burgoyne
([https://commons.wikimedia.org/wiki/File:17_mCi_Ac-225\(NO3\)3_at_ORNL_by_Dr_Andrew_R_Burgoyne.jpg](https://commons.wikimedia.org/wiki/File:17_mCi_Ac-225(NO3)3_at_ORNL_by_Dr_Andrew_R_Burgoyne.jpg)), [cropped]
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Wolverane (6)

This coordination polymer was first identified in the dental tissues of mammalian carnivores such as the spotted hyena, the wolverine and the Tasmanian devil.¹⁰ It's discoverer, Bert Whirlygig, was seeking the biochemical underpinnings of the incredible bite strength displayed by these bone-crushing critters. X-ray scattering experiments revealed the presence of titanium, which prompted Whirlygig probe further. He identified the outer layer of dental tissue as a series of adamantic acids cross-linked by titanium ions and fused to the enamel with a phosphate tag. Whirlygig named this tissue in honour of his supervisor, Thomas Wolverane.

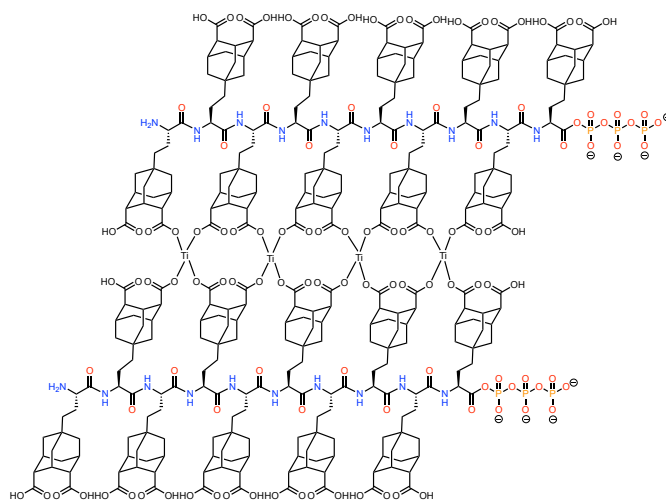
χ,ρ-Dimethylbyzantamine B (7)

χ,ρ-Dimethylbyzantamine B is a vibrant purple pigment produced in the flowers of *Orchis theodosius*, an paleoendemic orchid native to the regions of Anatolia and Thrace.¹¹ The

byzantamine core is derived from a collapsed porphyrin, and contains a nitrogen-centred radical. According to JACS 12:43, the radical is centred on all three apical nitrogens simultaneously, due to the rapid interconversion of the three constituent ecclesiastomers. An extract of the flowers of *O. theodosius* were used by the Byzantines to illuminate the holy scriptures, but the last specimens were thought to have been destroyed in the fall of Constantinople. A tiny enclave of surviving specimens was found on the slopes of Mr Ararat late in 2022, which were harvested to extract the pigment. The extraction was successful, and the structure of χ,ρ -Dimethylbyzantamine B was determined. This was fortuitous, because *O. theodosius* is now extinct (for sure, this time).

α -Malallenolanal (8)

α -Malallenolanal holds the dubious honour of being a compound that is just as hard to pronounce as it is to isolate. It was obtained from a bacterium native to Lake Malawi, *Bacillus kudzipha*. It interrupts a vital Na^+ ion transporter in a competing bacterium, *Legolactobacillus gimilii*.¹² Unfortunately, *B.*



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Wolverane

Figure 6: A pentamer of the polymer wolverane. The titanium ions crosslink the strands, strengthening the lattice.

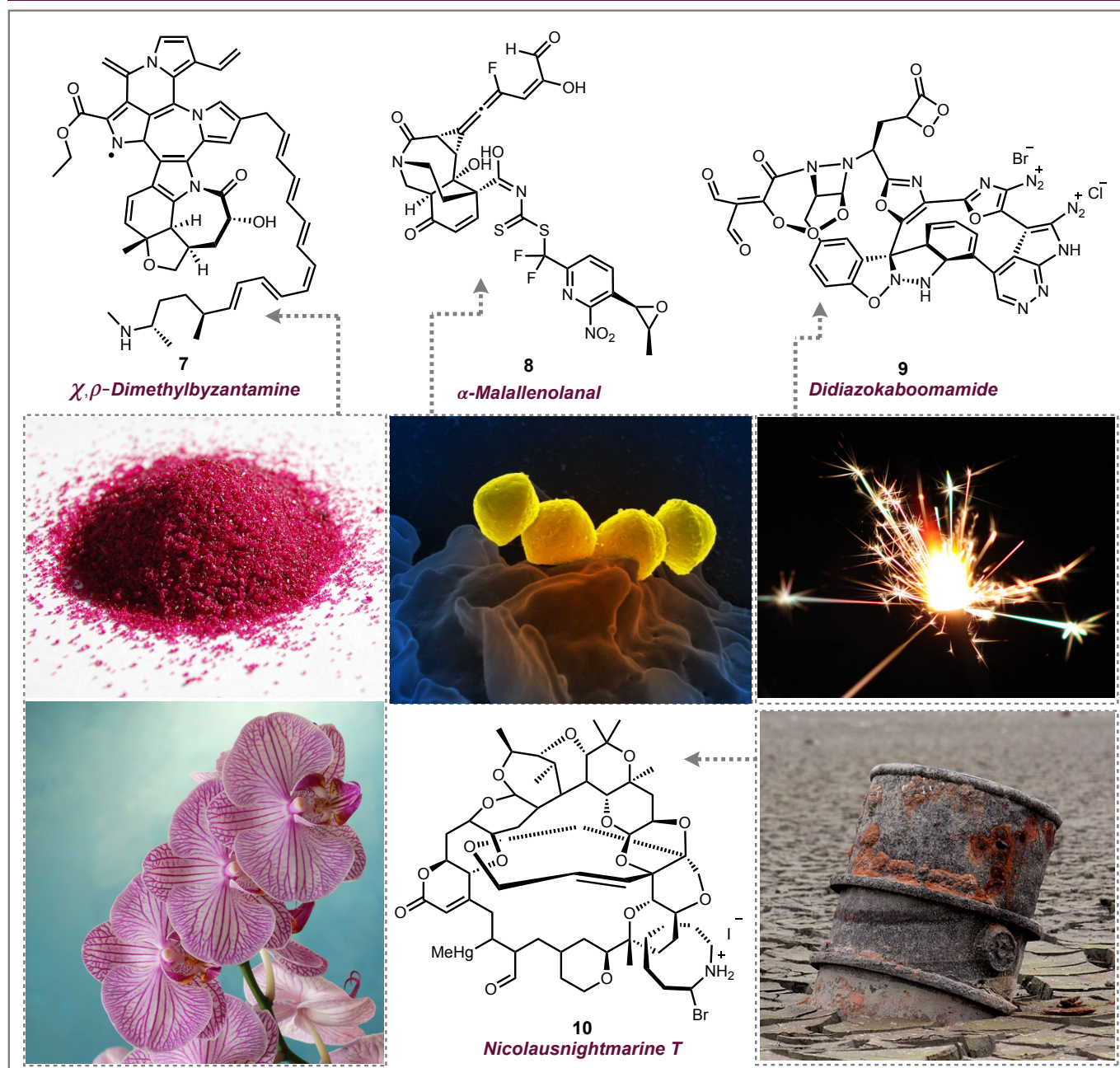


Figure 7: Left) the flowers of *O. theodosius*, (now extinct) and the refined byzantamine extract. Centre) A cluster of *B. kudzipha* expressing mallallenolanal. Right) Pure didiazokaboomamide at 7 K. Lower right) A drum of laboratory waste, from which nicolausnightmarine was isolated.

Kudzipha relies on the same Na⁺ ion transporter, making it quite a short-lived species. When released from the cell, α -malallenolanal has a half-life of ~2 seconds before catastrophic hydrolysis takes place. If the molecule reaches another organism within 2 seconds, nucleophilic attack on the pendant allene by an amine residue causes the molecule to fragment like an atomic hand grenade, irreversibly inhibiting its target enzyme, or anything else for that matter.

Didiazokaboomamide (9)

This notoriously capricious compound is produced by the flowers of *Cardamine instabilis*, a Micronesian plant that grows near harpy colonies. It was first isolated by Pete “no-fingers” Smith in 2015, and was fully characterised by Sarah “sleeveless” Shingleton in 2018.^{13,14} A large-scale synthesis was being pursued by “headless” Barry Forbes in 2021 when he suffered his career-ending injury.¹⁵

Nicholausnightmarine T (10)

This fiendishly complex polycyclic alkaloid was isolated from a fungus (*Desperandum cultorem*) found growing in a container of laboratory waste and elemental mercury.¹⁶ The compound is most notable for displaying the rare phenomenon of refragofluorescence. That is, the compound emits visible light upon exposure to frustration, angst or irritation. This peculiar characteristic was first observed by its discoverer, Zacherick Pferdongelplatz, while he was in the process of isolating it. Pferdongelplatz had just TLCed 147 column fractions in search of Nicholausnightmarine T without success, when he noticed a glowing orange band near the top of his column. Stripping the column with DMF gave a fraction containing pure product, which reverted to a colourless solid as soon as he'd run an NMR on it. The mechanism by which this fluorescence occurs is not well understood. Nicholausnightmarine T is also notable as it

contains two of the longest observed covalent bonds in chemistry, at 5.98(4.1) and 6.07(4.96) Å, as determined by X-ray crystallography.

Maitococcin (11)

This molecular monstrosity is a dinoflagellate polyol-polyether, which structurally resembles the related compound maitotoxin, among other things. Akin to maitotoxin, maitococcin raises cytosolic calcium levels, but is selective for the CatSper ion channels. As such, a carefully administered dose of maitococcin may enhance sperm motility and promote fertilisation. This may be why the algae that produces it (*Gambierdiscus lotsototoxicus*) has been consumed for centuries as an aphrodisiac by practitioners of traditional Polynesian medicine. Care must be exercised in the selection of the algae, as the consequence of picking badly is an agonising death from maitotoxin poisoning. The discovery of maitococcin in 2023¹⁷ has relegated schlonkotoxin¹⁸ to the rank of second-largest natural product, so naturally we'll be tacking a methyl group onto this as soon as we acquire a sample. Casey Nicolaou has stated an intention to synthesise it, right after he finishes making maitotoxin.

Structural Reassignments

The structures of following supernatural products have been recently revised, thanks to the advent of modern techniques or more competent chemists.

Hydroxyetalene (ETOH, 12)

Hydroxy-Etalene (ETOH) occurs naturally in plant ligmacellulose. It was first isolated by E. T. Alia, who rendered down a pile of manuscripts in boiling carbon-tet in a fit of post-rejection pique, and stumbled across it.²¹ He originally characterised it as a polyaromatic hydrocarbon (PAH), but it was

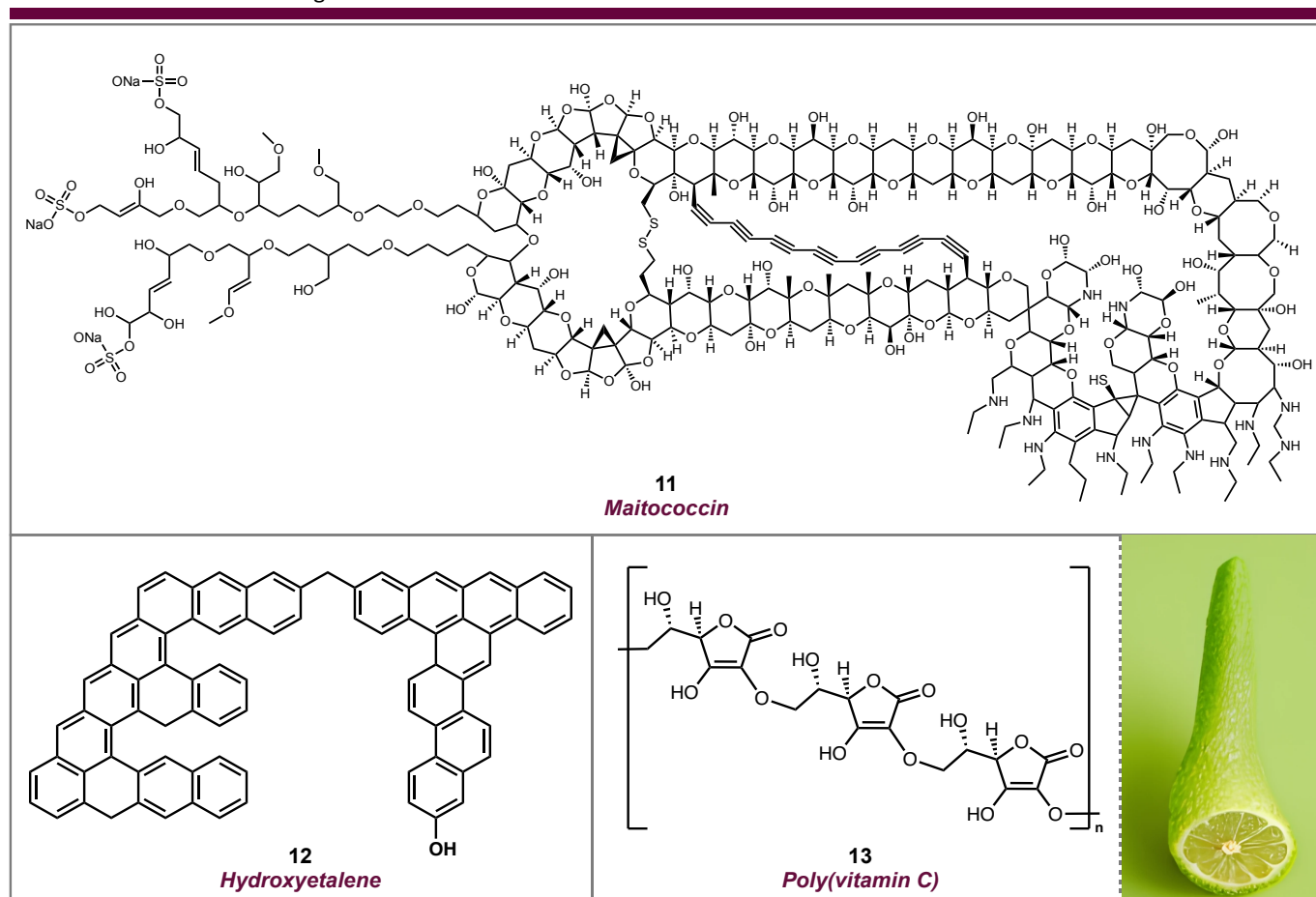


Figure 8: Top) The mighty maitococcin, most girthing of the natural products. Lower left) Hydroxyetalene (ETOH), a partially aromatic hydrocarbon. Lower Right) “Pauling’s polymer” and the Australian finger lime from which it was isolated. Inset image credit: Craiyon.com

reassigned as a mostly-aromatic hydrocarbon (MAH) last year, when Bernard Robdignag noticed a couple of extra hydrogens.²²

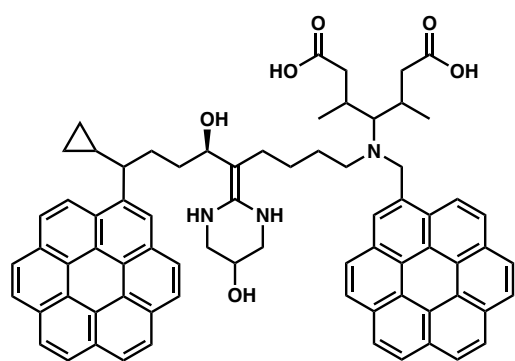
Poly(vitamin C) (13)

Known to many as “Pauling’s polymer” or “Vitamin C⁺⁺”, this molecule is formed in the flesh of the native Australian citrus, the finger lime. It transpires that as the lime elongates, so does the polymer and this is believed to enhance the panacea-like properties of vitamin C. Preliminary studies have found that the longer chain helps the vitamin permeate those hard-to-reach places in the body and stimulate antiviral activity in the extremities. This is particularly apparent in the treatment of the common cold - regular vitamin C is often ineffective as it cannot get past the nose hair and into the sinuses. Poly(vitamin C) doesn't suffer this same effect as the back of the chain can hold back the nose hairs while the front sneaks into the sinus and attacks the cold viruses directly. Linus Pauling didn't live to see the characterisation of poly(vitamin C), but if he had, he would almost certainly have loved it.^{22,5} Chemists only realised the compound was a polymer when they gave up on elemental analysis of finger lime samples, and used a real analytical technique to probe its structure.²³

Poly(vitamin C) is also believed to cross the blood-brain barrier and enhance the brain's computing power by settling into the various folds and wrinkles in the brain's surface. Modern studies even believe that if Gilbert Lewis had taken megadoses of 5 g of poly(vitamin C) each day that he would have won at least 3 Nobel prizes.

Bicyclopymidinol dicarboxylic acid A (14)

This supernatural product is produced by the “lunchbox fungus” (*C. Sphaerosperum*) which was discovered in 1999 by a group of high school students.²⁴ It was observed that the fungus could survive and thrive in extremely dry environments but until the isolation and characterisation of Bicyclopymidinol dicarboxylic acid A, this trait could not be rationalised. Scholars from Fudgebuster University determined that Bicyclopymidinol dicarboxylic acid A is responsible for binding water molecules and moving them around the fungi cells on demand, thus controlling salt concentrations throughout the fungal colony.



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Bicyclopymidinol Dicarboxylic Acid A

Figure 9: Bicyclopymidinol dicarboxylic acid A, a molecular pump.

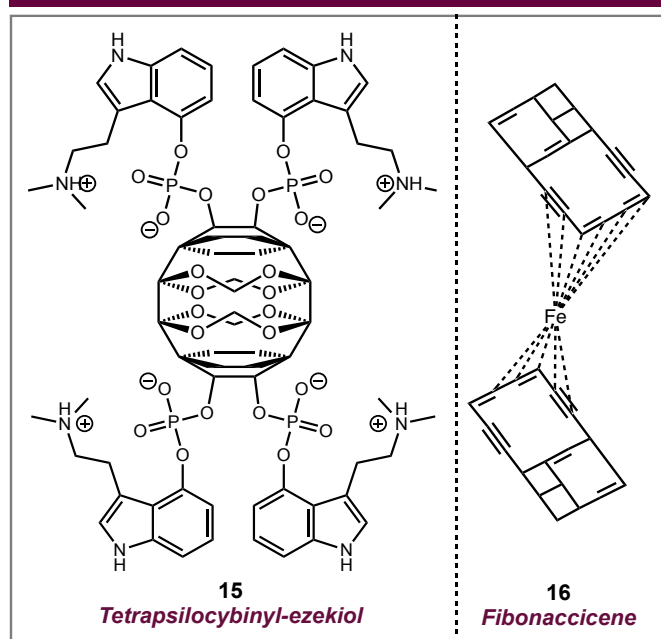
Tetrapsilocybinyl-ezekiol (15)

Tetrapsilocybinyl-ezekiol is a prodrug for psilocybin. It is produced by *C. supermyrrh*, a woody shrub native to the Sinai Peninsula. The ezekiol core is regarded by some as a “biblically accurate acetal”, while others postulate that Moses heard the voice of God after torching a patch of *C. supermyrrh* and inhaling the smoke. Naturally, these two incompatible viewpoints have been the subject of intense debates at IOUPAC meetings.

However, the name ezekiol was confirmed at the joint ACS Meeting–Burning Man festival in 2018.²⁵

Fibonacciene (16)

Chemists were baffled by the bonding within this molecule for decades. It was isolated from a bacterium inhabiting mine tailing dams in Western Australia.¹⁹ The bacterium (*Riotinitus bacillus*) has evolved to thrive in anaerobic mining sludge by substituting Fe³⁺ for oxygen in its cellular processes. It uses fibonacciene and the related β -hydroxyphenylbillitene as redox shuttles to oxidise its food: drilling lubricant. R.B. Woodward was trying to deduce its structure when he suffered his fatal heart attack in 1979. Whether this was correlation or causation will remain forever a mystery, but Woodward's death discouraged further attempts at the characterisation of Fibonacciene for 40 years. In 2019, a team of courageous chemists from Slapton grew crystals of fibonacciene by vacuum sublimation, and conclusively established the nature of the pi-system.²⁰



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Tetrapsilocybinyl-ezekiol

16

Fibonacciene

Figure 10: Two molecules that are both off their tits.

Conjectural Structures and Retractions

The following compounds are yet to be comprehensively characterised due to insufficient stability, insufficient access to the natural source, or insufficient competence on behalf of the chemists involved.

Cantsynthein I (17)

Cantsynthein I was detected in the coma of the comet C/2022 E3 (ZTF) in January of this year.²⁶ Convolution of the comet's spectral emission lines by chemputation has ambiguously determined the structure of this molecule. The comet's distinctive green glow has been attributed to the spin-discouraged Xe $\pi \rightarrow \pi^*$ transition.

Christmoxonium Hexahexafluorophosphate (18)

Christmoxonium hexahexafluorophosphate was published earlier this year, in a paper which claimed it to be the strongest acid ever reported.²⁷ This claim has since been disputed, as this compound was isolated and characterised using mass spectrometry alone. At no stage do the authors consider any other structure bearing the formula C₂₇H₂₇O₁₈. Instead, they calculate that their molecule would have a pKa of -37, assuming it existed for more than a nanosecond in a medium other than high vacuum.

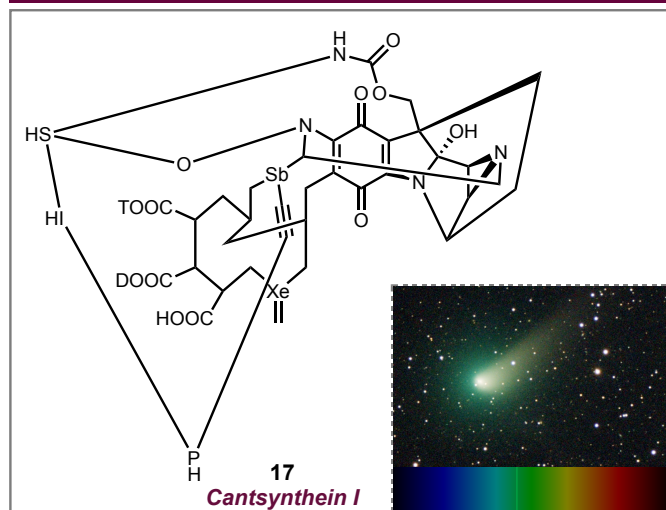
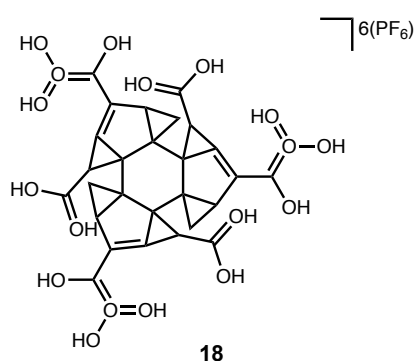


Figure 11: Comet C/2022 E3 (ZTF) (inset), gets its green coma from the excitation of Xe in cantsynthein I.



Christmoxonium Hexahexafluorophosphate

Figure 12: Structural assignment of 18, based on mass spectrometry.

Skaldinium IX (19)

The structure of Skaldinium IX was published in November 2022.²⁸ It was retracted in December of the same year, after it was found that the computational chemist who had calculated its geometry had been less than rigorous in the selection of their basis sets. To expedite their computations, the authors had selected the 1-11A# basis set, which ignores the contribution of inner shell electrons, protons, and electrostatics in general. It instead approximates the valence electrons as miniscule tennis balls attached to an atomic totem-poll by some simplified string-theory.

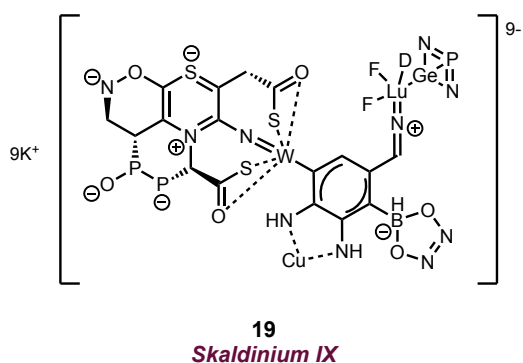


Figure 13: This is what happens to chemists who don't look after their basis sets.

Chernobylamine 2 (20)

While exploring beneath the wreckage of Chernobyl, Piter Khleb took some swabs from the melted mass of uranium and sand known as the "elephant's foot". Then he shot it with an AK-47,

for good measure. Dr Khleb plated out his swab samples, lysed the resultant cultures and extracted a luminescent compound.²⁹ Khleb's laboratory notebooks are still highly radioactive, but it appears he had proposed a structure featuring a preposterous uranium-uranium quadruple bond. This may have been the radiation sickness talking, as Khleb expired shortly afterwards. When another team of scientist entered his lab 20 years later, they found that the original culture of *R. diabolus* was still going strong, and appeared to be crawling towards the door. Quite reasonably, this team opted to avoid handling *R. diabolus*, and instead characterised the molecule *in vivo* with an IR spectrometer on the end of a stick.³⁰

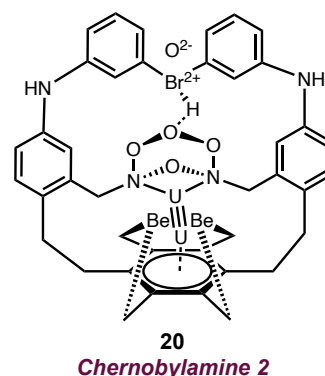


Figure 14: Did someone say bond angles?

Conclusion

Significant progress has been made in the isolation and characterisation of supernatural products. To translate this progress into real-world benefit, practical syntheses of these molecules are required.

Acknowledgements

G.S. acknowledges the contributions of his fellow immaterial scientists, for bringing these remarkable molecules to his attention.

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