No. 2020-11

School of Life Sciences
Seminar Series

Thursday
4:00 PM

3 December

Online Seminar
Zoom ID 315 451 8934 (Password: 101320)

Analysis of phototoxin taste closely correlates nucleophilicity to type 1 phototoxicity

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Abstract

Although pigment molecules, which exhibit colors by photo-absorbing specific wavelengths via pi-bond electron conjugation, often show toxicity due to generation of free radicals and reactive oxygen species (ROS) upon photo-illumination, the molecular mechanism by which organisms perceive phototoxins for avoidance is unknown. Here, we discover that nucleophile-sensing Transient Receptor Potential Ankyrin 1-A isoform (TRPA1(A)), previously shown to serve as a receptor for free radicals and ROS induced by photochemical reactions, enables Drosophila melanogaster to aphotically taste potentially phototoxic pigments for feeding deterrence. Thus, TRPA1(A) works for both cause (phototoxins) and effect (free radicals and ROS) of photochemical reactions. The pigment molecules, riboflavin, methylene blue, rose bengal and porphines, activate TRPA1(A) in darkness, and, upon light illumination, are able to initiate acrylamide polymerization, a consequence of free radical generation as known with type 1 phototoxins. On the other hand, other tested pigments are little capable of either task. Such pre-photochemical detection of phototoxins requires the nucleophile-sensing ability of TRPA1, since the phototoxin-induced activities of nucleophile-insensitive TRPA1 variants, such as the TRPA1(B) isoform and site-specific TRPA1(A) mutants, were much attenuated. When heterologously expressed in Xenopus oocytes, TRPA1(A) from the malaria-transmitting mosquito, Anopheles gambiae, shows larger current responses to phototoxins than Drosophila TRPA1(A), consistent with their previously characterized disparate nucleophile responsiveness. Collectively, in addition to detection of light-induced free radicals, nucleophile sensitivity of TRPA1(A) allows insects to minimize photochemical injuries through aphotic detection of phototoxins. Conversely, pigments need to bear high nucleophilicity (electron-donating propensity) to act as type-I phototoxins, which is consistent with the fact that transferring photo-excited electrons from phototoxins to other molecules causes free radicals. Thus, identification of a novel sensory mechanism in Drosophila reveals a property fundamental to type-I phototoxins.