Understanding the pathways involved in chlorophyll breakdown provides a molecular map to the color changes observed in plant life on a global scale each fall. Surprisingly, little is known about the fate of phytol, chlorophyll’s 20-carbon branched-chain tail, during this process. A recent study from Gutbrod et al. provides evidence using physiological, genetic, and exquisitely sensitive analytical approaches that phytanoyl is an intermediate in plant phytol catabolism. These insights and techniques open the door to further investigation of this complicated metabolic system, with implications for plant health and agriculture.

Most life on earth depends on photosynthesis, which depends on the pigment chlorophyll. Chlorophyll turns over during the life of plants, and degradation is particularly rapid when leaves senesce or when plants experience specific stresses, such as salt exposure, nitrogen deprivation, or extended darkness, that induce chlorosis. Chlorophyll breakdown enables recycling of its components, including its phytol side chain. However, the turnover pathway of the phytol side chain has been difficult to determine as one suspected intermediate is both toxic to cells, limiting its accumulation by artificial means, and prone to modification during extraction. In their study, Gutbrod et al. (1) now present a strong case for the existence of this degradative pathway in plants. They first established a gas chromatography–MS method capable of detecting phytanoyl in nitrogen-deprived Arabidopsis thaliana leaves. Their experimental approach required identification of a suitable agent to derivatize and thus stabilize the aldehyde. Using these methods, they demonstrated that phytanoyl did not accumulate in a mutant blocked in pheophorbide synthesis. Notably, the formation of phytenal occurred in boiled plants to about half the extent that it occurred in living plants, suggesting that the formation of phytenal may occur by a nonenzymatic mechanism, as well as via an enzymatic one. Finally, Gutbrod et al. (1) examined the relative proportions of phytanoyl and the known derivatives of phytol, finding that phytanoyl is a minor component of chlorophyll breakdown and phytenal synthesis. Notably, the formation of phytenal occurred in boiled plants to about half the extent that it occurred in living plants, suggesting that the formation of phytenal may occur by a nonenzymatic mechanism, as well as via an enzymatic one. Finally, Gutbrod et al. (1) examined the relative proportions of phytanoyl and the known derivatives of phytol, finding that phytanoyl is a minor component of chlorophyll breakdown and phytenal synthesis.
phytenal in plants occurs via the mammalian pathway, it is possible that the catabolism of phytenal cannot be detected due to downstream derivatives found in plant metabolites. However, as Gutbrod et al. described in mammals, orthologous plant enzymes might serve as candidates. Nevertheless, the degradative pathway for phytol has been shown to be blocked by mutations, indicating that the three pathways compete for phytol substrate. If the degradative pathway for phytol from chlorophyll metabolism, the identification of the enzymes involved also will help determine the subcellular location of phytol degradation. In mammals, the initial steps of the pathway to degrade phytanoyl-CoA (α-oxidation and first rounds of β-oxidation) take place in the peroxisome, followed by further breakdown of the chain in the mitochondrion.

A suggestion that a phytol degradative pathway may play an important role in the life of a plant comes from work showing that mutations in a gene leading to accumulation of phytanoyl-CoA result in the inability of plants to survive extended darkness as well as WT plants do (9). The gene of interest encodes a mitochondrial protein, electron-transfer flavoprotein:ubiquinone oxidoreductase, which seems to be important for catabolism of a variety of substrates and may therefore offer an additional clue to establishing a full metabolic pathway. The new analytical tools established by Gutbrod et al. open the door to much needed research on this fascinating system. Given that phytol breakdown is key to the synthesis of antioxidant pigments and vitamins in certain fruits and seeds, understanding the multiple fates of phytol has the potential to increase our ability to ensure that crop plants are resilient to chlorotic stresses and able to produce nutritious food.

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Conflict of interest—The authors declare that they have no conflicts of interest with the contents of this article.

Abbreviations—The abbreviations used are: CoA, Coenzyme A.

Figure 1. Multiple fates for phytol after removal from chlorophyll. During chlorophyll degradation, phytol is cleaved from the chlorin ring. Previous work has shown that this released phytol can be sequestered as phytol esters or used to synthesize tocopherols or phylloquinone. The phytol group in phytol diphosphate also can be recycled into chlorophyll by reaction with chlorophyllide a (not shown). Gutbrod et al. (1) use improved analytical methods to detect phytenal, suggesting that phytol can also be degraded in plants.

component of the overall pool, with the majority of the carbon being funneled into tocopherol and fatty acid phytol ester synthesis. However, the authors also demonstrated that production of phytenal is enhanced when flux through either of these synthetic pathways is blocked by mutations, indicating that the three pathways compete for phytol substrate.

Questions remain about the reactions in the degradative pathway for phytol from chlorophyll metabolism, the identities of the enzymes that catalyze them, and their subcellular locations. It is also unclear whether this pathway serves to metabolize significant amounts of phytol from breakdown of phytol esters, which decrease in amount when chlorotic stresses are relieved (7). The mechanism of the conversion of phytol to phytenal in particular remains ambiguous, as it seems to be at least partially nonenzymatic. Previous work had suggested a photooxidative reaction (10), but that is unlikely to be the only mechanism because Gutbrod et al. (1) show that phytenal can be produced during extended darkness. Because the degradative pathway for phytol has been described in mammals, orthologous plant enzymes might offer obvious candidates. However, as Gutbrod et al. (1) did not detect the downstream derivatives of phytenal found in the mammalian pathway, it is possible that the catabolism of phytenal in plants occurs via a novel pathway. On the other hand, such metabolites might be extremely transient and therefore difficult to detect. Knowing the identity of the enzymes involved also will help determine the subcellular location of phytol degradation. In mammals, the initial steps of the pathway to degrade phytanoyl-CoA (α-oxidation and first rounds of β-oxidation) take place in the peroxisome, followed by further breakdown of the chain in the mitochondrion.

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