SPOROPOLLENIN

The makeup of a gamete space capsule

Sporopollenin, which encapsulates gametes in spore and pollen grains, is probably the most chemically inert biopolymer. This inertness is essential for gamete protection, but also hinders the elucidation of sporopollenin molecular structure. Now, the macromolecular network forming sporopollenin is described in unprecedented detail.

Paula Guzmán-Delgado and Maciej A. Zwieniecki

The establishment of plants on land, about 450 million years ago, is one of the most significant episodes in life evolution, with far-reaching impacts that shaped the global ecosystem. The transition from aquatic or semi-aquatic environments — where plant ancestors (green algae) grew — into permanent terrestrial conditions presented a great challenge for plants, resulting in the evolution of concomitant adaptive changes. Sporopollenin, the major constituent of the outer cell wall (exine) of spores and their homologue, pollen, presumably played a key role in facilitating this transition by furnishing an optimal encapsulation of plant gametes that enabled dispersal and sexual reproduction. Sporopollenin is extremely resistant to physical and chemical degradation, probably more so than any other plant product[1]. This high resistance has also likely contributed to the preservation of spores and pollen in the fossil record, providing extensive and continuous records over geological time, including evidence of the first land plants[2]. However, such recalcitrance also results in difficulties in accurately determining its chemical composition and ultrastructure, which renders sporopollenin the least-known plant polymer[3]. In this regard, several studies suggest a polymeric structure for sporopollenin, potentially having both aliphatic and aromatic components, but the specific nature of its molecular constituents and inter-molecular linkages are poorly understood[4,5]. Now, in a paper published in *Nature Plants*, Li et al.[6] shed new light on the fine structure of sporopollenin.

Li et al.[6] developed a methodology that combines optimized traditional procedures for biopolymer analysis with innovative techniques aimed at unravelling the sporopollenin molecular structure. The authors were able to deduce the structure of pitch pine pollen sporopollenin with an extraordinary level of detail. Sporopollenin was inferred to be mainly constituted of two fatty-acid-derived polyvinyl alcohol (PVA)-like units (relatively long polyhydroxylated aliphatic molecules), each flanked at one end by an α-pyrone moiety and crosslinked at the other end through an ester group. The PVA units are crosslinked by 7-*O*-*p*-coumaroylated aliphatic units composed of 16 carbon atoms through an *m*-dioxane moiety that features an acetal. The PVA-like units are probably linked through ether bonds with glycerol-like moieties, and minor amounts of naringenin. Concerning the relative abundance of sporopollenin chemical constituents, the *p*-coumaroylated aliphatic units and PVA-like units are the main products of sporopollenin 'soluble' and non-degradative fractions, respectively, and the proportion of carbon is higher in aliphatic domains than in aromatic ones. While this is the average structure of pine sporopollenin based on the ^{13}C nuclear magnetic resonance spectra, its native structure is likely to be more heterogeneous, especially in terms of inter-molecular crosslinking.

The presence of two major types of linkages in pine sporopollenin (ester and acetal) is likely to confer sporopollenin with a higher resistance to decay as opposed to other plant polymers that may contain a single major linkage type. Moreover, the identification of α-pyrone, *p*-coumarate and naringenin moieties as integral constituents of sporopollenin, supports sporopollenin's essential function in protecting gametes against ultraviolet radiation, and provides insight into biosynthetic mechanisms.

The molecular structure of sporopollenin has been a matter of interest for a long time[7], and the investigation by Li et al.[6] may have profound implications for both the fundamental and applied viewpoints. First, given the extensive fossil record of spores and pollen, as well as their ubiquitous presence in current land plants, the analysis of sporopollenin from different sources may offer essential information to understand Earth's history (since the first algae bearing sporopollenin[8]), and to predict future scenarios. In this sense, the heterogeneity of sporopollenin can be interpreted as a fundamental feature that may provide both the polymer and the cell wall a certain degree of dynamism, and thus the ability to adapt to (and reflect) different conditions. Second, determining the molecular structure of sporopollenin will contribute to our understanding of the biosynthetic machinery that allowed plant terrestrialization[1,9]. Finally, unravelling the structure of perhaps the most resistive biopolymer is likely to help the design of biomimetic products with such long-lasting desired properties. Again, the heterogeneous nature of sporopollenin and associated molecules confers exines a wide range of physico-chemical properties. Exines can serve as microparticles and microcapsules for a number of applications, from metal remediation to oral vaccination[3]. Thus, the development of a standardized, consistent methodology that allows the identification of sporopollenin molecular structure is a breakthrough in diverse research fields. Additional studies using sporopollenin from different plant species and material should be performed to test the replicability of the method by Li et al.[6]. ❐

Paula Guzmán-Delgado* and Maciej A. Zwieniecki

Department of Plant Sciences, University of California Davis, Davis, CA, USA.

**e-mail: pguzmandelgado@ucdavis.edu*

Published online: 17 December 2018
https://doi.org/10.1038/s41477-018-0342-3

References

1. Niklas, K. J., Cobb, E. D. & Matas, A. J. *J. Exp. Bot.* **19**, 5261–5269 (2017).
2. Wellman, C. H. & Strother, P. K. *Palaeontology* **58**, 601–27 (2015).
3. Mackenzie, G., Boa, A. N., Diego-Taboada, A., Atkin, S. L. & Sathyapalan, T. *Front. Mater.* **2**, 66 (2015).
4. Domínguez, E., Mercado, J. A., Quesada, M. A. & Heredia, A. *Sex. Plant Reprod.* **12**, 171–178 (1999).
5. Jardine, P. E., Abernethy, F. A., Lomax, B. H., Gosling, W. D. & Fraser, W. T. *Rev. Palaeobot. Palyno.* **238**, 1–6 (2017).
6. Li, F. S., Phyo, P., Jacobowitz, J., Hong, M. & Weng, J. K. *Nat. Plants*. https://doi.org/10.1038/s41477-018-0330-7 (2019).
7. Shaw, G. in *Sporopollenin* (eds Brooks, J. et al.) 305–350 (Academic Press, London, 1971).
8. Atkinson, J. A., Gunning, B. E. & John, P. C. *Planta* **107**, 1–32 (1972).
9. Daku, R. M. et al. *PLoS ONE* **11**, e0146817 (2016).

Competing interests

The authors declare no competing interests.