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## Data Article

# An FT-IR and XPS spectroscopy dataset of *Pinus ponderosa* sporopollenin and related samples to elucidate sporopollenin structural features



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## ABSTRACT

The ATR FT-IR spectra of *Pinus ponderosa* sporopollenin isolated from pollen spores by enzymatic digestion. Sporopollenin is also isolated by solvent extraction, followed by either acidolysis with phosphoric acid, and acetolysis is reported [1]. The FT-IR spectra are supplemented by XPS data of the isolated sporopollenin samples. The enzymatically isolated sporopollenin is subjected to a variety of chemical treatments and modifications, including alkaline hydrolysis, deuteration (by both D<sub>2</sub>O and methanol-d<sub>4</sub>), sodium cyanoborohydride reduction, hydrolysis by peracetic acid, bromination, acetylation with acetone and octanal, and acid-catalyzed ketal cleavage. The sporopollenin isolated by acidolysis and acetolysis are also subjected to alkaline hydrolysis. The sporopollenin samples are compared to a variety of model compounds representative of putative structural constituents and functional groups.

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Specifications Table

|                                |  |
|--------------------------------|--|
| Subject                        | Agricultural and Biological Science: Plant Science   |
| Specific subject area          | Composition of the plant-derived biopolymer sporopollenin  |
| Type of data                   | FT-IR spectra and X-ray photoelectron spectra  |
| How data were acquired         | Attenuated total reflectance Fourier transform infrared spectra was performed using a Nicolet iS50 FTIR spectrometer equipped with a Smart iTR ATR sampling accessory. X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics PE-5800 X-ray photoelectron spectrometer.   |
| Data format                    | Raw data after atmospheric suppression (ATR FT-IR)<br>Raw data (XPS)   |
| Parameters for data collection | Sporopollenin was isolated from <i>Pinus ponderosa</i> by several common procedures, and was chemically treated and modified. Reference compounds were used as received.   |
| Description of data collection | The ATR-FTIR instrument was operated with a DTGS/KBr detector and KBr beamsplitter (XT-KBr). Spectra were generated from 64 scans with a data spacing of $0.964\text{ cm}^{-1}$ over the range of $4000\text{ to }650\text{ cm}^{-1}$ . The XPS spectrometer used an Al K $\alpha$ X-ray source (1486.6 eV). Spectra were acquired in the range of $1100\text{--}10\text{ eV}$ with a pass energy of $187.85\text{ eV}$ and a step size of $1.6\text{ eV}$ at a take-off angle of $45^\circ$ . |
| Data source location           | Colorado State University<br>Fort Collins, Colorado<br>USA   |
| Data accessibility             | Data are provided as supplementary files with the article.   |
| Related research article       | Author's name: Lutzke, A., Morey, K.J., Medford, J.I. and Kipper, M.J<br>Title: Detailed characterization of <i>Pinus ponderosa</i> sporopollenin by infrared spectroscopy<br>Journal: <i>Phytochemistry</i><br><a href="https://doi.org/10.1016/j.phytochem.2019.112195">https://doi.org/10.1016/j.phytochem.2019.112195</a>  |

#### Value of the Data

- The chemical structure of sporopollenin is unknown; these data can be used to test hypotheses about sporopollenin structure.
- Biologists, chemists, and materials scientists might use these data to infer the structure of sporopollenin, and to elucidate structure-function-property relationships.
- Future studies of sporopollenin structure by FT-IR and other techniques could use these data as a reference; future studies might refine band assignments to particular functional groups.

## 1. Data

The dataset contains both XPS and FT-IR data of sporopollenin from *Pinus ponderosa* pollen exine. The sporopollenin was isolated from the pollen by three different treatment protocols (enzymatic digestion, acidolysis, and acetolysis) [1]. To further elucidate spectroscopic features, the sporopollenin isolated by all three procedures was treated with potassium hydroxide. FT-IR spectra are also included for the enzymatically isolated sporopollenin after deuteration (with methanol- $d_4$  and  $D_2O$ ), amination (with sodium cyanoborohydride), oxidation (with peracetic acid), bromination (with bromine in chloroform and water), and acetalization (with acetone in the presence or absence of iodine, and with octanal in the presence of iodine). FT-IR spectra are also included for the acetone and octanal ketal products further hydrolyzed, by hydrochloric acid and bromine, respectively. The FT-IR spectra of several reference compounds containing either putative sporopollenin substituents or representative functional groups are also reported. These include aliphatic saturated and unsaturated fatty acids (stearic and oleic), a fatty acid ester (glycerol trioleate), several cinnamic acids, *n*-octane, octanal, 5-nonanol, 1-hexadecanol,  $\beta$ -carotene, 4-hydroxy-6-methoxy-2-pyrone, and di-*n*-hexyl ether. The FT-IR spectra of other reference polymers are also reported, including commercially available *Pinus* pollen, *Lycopodium* sporopollenin, poly(vinyl alcohol), citrus pectin, cellulose, and deuterated cellulose.

The XPS data are provided in the Supplementary Data as both comma-separated variables and in the PHI Multipak spe format. The samples and corresponding filename prefixes are listed in Table 1.

**Table 1**

XPS samples and sample designations provided in the Supplementary Data.

| sample  | filename prefixes and sample IDs      |
|---|---------------------------------------|
| enzymatically isolated, before water rinse                      | R-1.01a (1); R-1.01a (2); R-1.01a (3) |
| enzymatically isolated, after 72 h water rinse                  | R-1.02 (1); R-1.02 (2); R-1.02 (3)    |
| enzymatically isolated, after 144 h water rinse                 | R-1.02a (1); R-1.02a (2); R-1.02a (3) |
| enzymatically isolated, after KOH treatment                     | R-1.03 (1); R-1.03 (2); R-1.03 (3)    |
| solvent extracted, before <i>A. oryzae</i> protease proteolysis | R-2.01 (1); R-2.01 (2); R-2.01 (3)    |
| solvent extracted, after <i>A. oryzae</i> protease proteolysis  | R-2.02 (1); R-2.02 (2); R-2.02 (3)    |
| after acidolysis  | R-3.01 (1); R-3.01 (2); R-3.01 (3)    |
| after acetyolysis   | R-4.01 (1); R-4.01 (2); R-4.01 (3)    |
| carbon tape   | R-5.22                                |
| <i>Lycopodium</i> sporopollenin (commercial source)             | R-5.02 (1); R-5.02 (2); R-5.02(3)     |

ATR FT-IR data are organized into five groups and provided in the Supplementary data. The five groups of spectra and the corresponding filename prefixes and sample identification numbers are listed in [Table 2](#).

## 2. Experimental design, materials, and methods

### 2.1. Materials

Glyceryl trioleate (99%) and sodium cyanoborohydride (95%) were obtained from Acros Organics (Morris Plains, NJ, USA). Acetic anhydride (>97%), bromine (99.8%),  $\beta$ -carotene (99%), citrus pectin, di-*n*-hexyl ether (98%), 1-hexadecanol (98%), *trans*-4-hydroxycinnamic acid (98%), *trans*-4-hydroxy-3-methoxycinnamic acid (99%), 4-hydroxy-6-methyl-2-pyrone (98%), iodine (>99.99%), *trans*-4-methoxycinnamic acid (98%), microcrystalline cellulose, 5-nonanol (98%), octanal (98%), and oleic acid (99%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Peracetic acid solution (32% w/w in dilute acetic acid) and protease from *Aspergillus oryzae* were obtained from Sigma-Aldrich (St. Louis, MO, USA). Methyl *trans*-4-hydroxycinnamate (>98.0%) and stearic acid (>98.0%) were obtained from TCI America (Portland, OR, USA). Cellulase and Macerozyme R-10 were obtained from Yakult Pharmaceutical Industry Co, Ltd. (Tokyo, Japan). Sporopollenin (*Lycopodium*) was purchased from Poly-science, Inc. (Warrington, PA, USA). Pollen from *Pinus ponderosa* was purchased from the Canadian Pine Pollen Company (North Vancouver, BC, Canada). The pollen was harvested during May and June of 2017 in Merritt, BC, Canada, and was sifted through 200 mesh and dehydrated by solar dryer prior to use. Deionized water (18.2 M $\Omega$  · cm) was supplied by a Milli-Q Synthesis A10 water purification system.

### 2.2. Methods

#### 2.2.1. Infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Nicolet iS50 FTIR spectrometer equipped with a Smart iTR ATR sampling accessory and a diamond crystal plate (Thermo Fisher Scientific, Madison, WI, USA). The instrument was operated with a DTGS/KBr detector and KBr beamsplitter (XT-KBr). Spectra were generated from 64 scans with a data spacing of 0.964 cm<sup>-1</sup> over the range of 4000 to 650 cm<sup>-1</sup>. Spectra were processed (atmospheric suppression; ATR correction was not applied) and band positions were obtained using the OMNIC software suite.

#### 2.2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics PE-5800 X-ray photoelectron spectrometer with an Al K $\alpha$  X-ray source (1486.6 eV) (Chanhasen, MN, USA). Samples were stored in a desiccator prior to analysis and were distributed as a densely packed layer on double-sided carbon tape. Spectra were acquired in the range of 1100–10 eV with a pass energy of 187.85 eV and a step size of 1.6 eV at a take-off angle of 45°.

**Table 2**

ATR FT-IR samples and sample designations provided in the Supplementary Data.

| sample  | filename prefixes and sample ID(s) |
|---|------------------------------------|
| Group R-1: All samples were sporopollenin prepared by enzymatic isolation from <i>P. ponderosa</i> pollen |                                    |
| before extraction with organic solvents   | R-1.01 (1); R-1.01 (2); R-1.01 (3) |
| after extraction with organic solvents  | R-1.02 (1); R-1.02 (2); R-1.02 (3) |
| after KOH treatment   | R-1.03 (1); R-1.03 (2); R-1.03 (3) |
| after D <sub>2</sub> O treatment  | R-1.04 (1); R-1.04 (2); R-1.04 (3) |
| after methanol-d <sub>4</sub> treatment (72 h)  | R-1.05 (1); R-1.05 (2); R-1.05 (3) |
| after methanol-d <sub>4</sub> treatment (144 h)   | R-1.06 (1); R-1.06 (2); R-1.06 (3) |
| after sodium cyanoborohydride treatment   | R-1.07(1); R-1.07 (2); R-1.07 (3)  |
| after peracetic acid treatment (low concentration)  | R-1.08 (1); R-1.08 (2); R-1.08 (3) |
| after peracetic acid treatment (high concentration)   | R-1.09 (1); R-1.09 (2); R-1.09 (3) |
| after treatment with Br <sub>2</sub> (in chloroform)  | R-1.10 (1); R-1.10 (2); R-1.10 (3) |
| after treatment with Br <sub>2</sub> (in pH 5.0 buffer)   | R-1.11 (1); R-1.11 (2); R-1.11 (3) |
| after treatment with acetone (with I <sub>2</sub> )   | R-1.12 (1); R-1.12 (2); R-1.12(3)  |
| after treatment with acetone (without I <sub>2</sub> )  | R-1.13 (1); R-1.13 (2); R-1.13 (3) |
| sporopollenin-acetone ketal treated with HCl  | R-1.14 (1); R-1.14 (2); R-1.14(3)  |
| after treatment with octanal (with I <sub>2</sub> )   | R-1.15 (1); R-1.15 (2); R-1.15(3)  |
| sporopollenin-octanal ketal treated with Br <sub>2</sub>  | R-1.16 (1); R-1.16 (2); R-1.16(3)  |
| Group R-2: Samples treated by solvent extraction to prepare for acidolysis and acetolysis                 |                                    |
| before proteolysis with <i>A. oryzae</i> protease   | R-2.01 (1); R-2.01 (2); R-2.01 (3) |
| after proteolysis with <i>A. oryzae</i> protease  | R-2.02 (1); R-2.02 (2); R-2.02 (3) |
| Group R-3: Samples treated by acidolysis with phosphoric acid   |                                    |
| after H <sub>3</sub> PO <sub>4</sub> treatment  | R-3.01 (1); R-3.01 (1); R-3.01 (3) |
| after KOH treatment   | R-3.02 (1); R-3.02 (2); R-3.02 (3) |
| Group R-4: Samples treated by acetolysis with acetic anhydride and concentrated sulfuric acid             |                                    |
| after acetolysis  | R-4.01 (1); R-4.01 (2); R-4.01 (3) |
| after KOH treatment   | R-4.02 (1); R-4.02 (2); R-4.02 (3) |
| Group R-5: Reference samples  |                                    |
| <i>P. ponderosa</i> pollen  | R-5.01 (1); R-5.01 (2); R-5.01 (3) |
| <i>Lycopodium</i> sporopollenin (commercial source)   | R-5.02                             |
| oleic acid  | R-5.03                             |
| glycerol trioleate  | R-5.04                             |
| <i>trans</i> -4-hydroxycinnamic acid  | R-5.05                             |
| <i>trans</i> -4-hydroxycinnamic acid (deuterated by methanol-d <sub>4</sub> )                             | R-5.06                             |
| <i>n</i> -octane  | R-5.07                             |
| stearic acid  | R-5.08                             |
| poly(vinyl alcohol)   | R-5.09                             |
| octanal   | R-5.10                             |
| <i>trans</i> -4-hydroxy-3-methoxycinnamic acid  | R-5.11                             |
| β-carotene  | R-5.12                             |
| 5-nonanol   | R-5.13                             |
| microcrystalline cellulose  | R-5.14                             |
| <i>trans</i> -4-methoxycinnamic acid  | R-5.15                             |
| methyl <i>trans</i> - <i>p</i> -coumarate   | R-5.16                             |
| 4-hydroxy-6-methoxy-2-pyrone  | R-5.17                             |
| 1-hexadecanol   | R-5.18                             |
| citrus pectin   | R-5.19                             |
| deuterated cellulose  | R-5.20                             |
| di- <i>n</i> -hexyl ether   | R-5.21                             |

### 2.2.3. Isolation of sporopollenin by enzymatic digestion of the *P. ponderosa* pollen intine (R-1.01, R-1.01a, R-1.02, and R-1.02a)

*Pinus ponderosa* pollen (500 mg;  $n = 3$ ) was suspended in 20 mL of deionized water and stirred continuously for 24 h. After this period had elapsed, the suspension was filtered through sintered glass and the pollen was washed with  $5 \times 10$  mL of deionized water, then re-suspended in 20 mL of 0.1 M sodium acetate buffer (pH 4.5) containing 1% w/v Cellulase and Macerozyme R-10 and stirred at 30 °C for 72 h to hydrolyze the pollen intine. Following the enzymatic digestion, the pollen suspension was filtered and the recovered solid washed with  $5 \times 10$  mL of deionized water, then stirred for an additional 24 h in 20 mL of deionized water at 30 °C. The solid was again isolated by filtration of the

suspension and washed with  $5 \times 10$  mL of deionized water,  $3 \times 10$  mL of methanol, and  $3 \times 10$  mL of diethyl ether. Five discrete 24 h extractions were performed in sequence by stirring the solid in 20 mL of diethyl ether, chloroform, methanol, 2-ethoxyethanol, or water. Between extractions, the pollen suspension was filtered and the recovered solid was washed with  $5 \times 10$  mL of the extraction solvent, followed by  $3 \times 10$  mL of the following solvent in the sequence. Once this procedure had been completed, the pollen was washed with  $10 \times 10$  mL of deionized water and dried under vacuum to yield  $130 \pm 7$  mg of putative sporopollenin as a pale yellow powder (**R-1.01a**). To remove nitrogenous contaminants and produce material suitable for spectroscopic analysis, sporopollenin was incubated in deionized water at  $40^\circ\text{C}$  for 72 h under constant agitation, recovered by centrifugation, and subsequently washed with  $3 \times 10$  mL of deionized water by repeated centrifugation (**R-1.02**). For XPS analysis the incubation in deionized water and washing was repeated for an additional 72 h (144 h total) (**R1.02a**). As a control experiment, the enzymatic digestion was repeated without extraction with organic solvents, following an otherwise identical protocol (**R-1.01**). ATR-FTIR: 3350, 3026 (est), 2926, 2855, 2741 (est), 2689 (est), 2621 (est), 1710 (est), 1680, 1630, 1605, 1588, 1556 (est), 1515, 1463 (est), 1437, 1411 (est), 1379, 1348 (est), 1323, 1308 (est), 1283 (est), 1261, 1233 (est), 1202, 1168, 1125 (est), 1103, 985, 943 (est), 912 (est), 833,  $720\text{ cm}^{-1}$ . ATR-FTIR (without solvent extraction): 3341, 3009, 2920, 2851, 2738 (est), 2687 (est), 2623 (est), 1737, 1706, 1682, 1630, 1605, 1588, 1551 (est), 1515, 1464 (est), 1438, 1411 (est), 1378, 1347 (est), 1323, 1309 (est), 1283 (est), 1262, 1232 (est), 1202, 1168, 1136 (est), 1103, 1044, 985, 939 (est), 911 (est), 832, 776 (est),  $719\text{ cm}^{-1}$ .

#### 2.2.4. Solvent extraction of *P. ponderosa* pollen (R-2.01)

To prepare *P. ponderosa* pollen for acidolysis with phosphoric acid or acetolysis, it was first extracted with a sequence of solvents to remove soluble organic compounds. *P. ponderosa* pollen (4.00 g) was suspended in 160 mL of deionized water and vigorously stirred for 24 h. The pollen suspension was filtered through sintered glass and the recovered solid was washed with  $5 \times 80$  mL of deionized water,  $3 \times 80$  mL of methanol, and  $3 \times 80$  mL of diethyl ether. Pollen was then stirred for 24 h in 160 mL of diethyl ether, 24 h in chloroform, and 48 h in methanol. Between each extraction, the pollen suspension was filtered and the solid was washed with  $5 \times 80$  mL of the extraction solvent, followed by  $3 \times 80$  mL of the following solvent in the sequence. After filtration, the solid was washed with  $5 \times 80$  mL of diethyl ether and methanol, then placed under vacuum to yield solvent-extracted *P. ponderosa* pollen as a pale yellow powder. ATR-FTIR: 3341, 3022 (est), 2926, 2855, 2740 (est), 2689 (est), 2630 (est), 1740 (est), 1706 (est), 1678, 1630, 1605, 1589, 1551 (est), 1515, 1463 (est), 1437, 1410 (est), 1378, 1348 (est), 1323, 1309 (est), 1283 (est), 1261, 1233 (est), 1203, 1168, 1136 (est), 1102, 1078, 1031, 991, 940 (est), 911 (est), 833, 775 (est),  $718\text{ cm}^{-1}$ .

#### 2.2.5. Isolation of sporopollenin by acidolysis of *P. ponderosa* pollen with phosphoric acid (R-3.01)

*P. ponderosa* pollen (200 mg;  $n = 3$ ) that had previously been extracted with organic solvent (*vide supra*) was suspended in 10 mL of 85% w/w phosphoric acid. The resulting suspension was stirred at  $50^\circ\text{C}$  for 72 h, then the solid was isolated by filtration through sintered glass. The pollen was washed with  $5 \times 10$  mL of 85% w/w phosphoric acid,  $10 \times 10$  mL of deionized water, and  $3 \times 10$  mL of methanol, then washed with an additional  $3 \times 10$  mL of deionized water by repeated centrifugation and disposal of the supernatant. The resulting solid was placed under vacuum to yield  $81 \pm 1$  mg of putative sporopollenin as a light brown powder. ATR-FTIR: 3384, 3026 (est), 2926, 2855, 2736 (est), 2689 (est), 2626 (est), 1775 (est), 1702, 1680 (est), 1632, 1614, 1607, 1590 (est), 1516, 1493 (est), 1462 (est), 1437, 1404, 1380, 1342, 1324 (est), 1307 (est), 1273 (est), 1236, 1204, 1170, 1129, 1107, 1074, 1006, 937 (est), 833, 777,  $722\text{ cm}^{-1}$ .

#### 2.2.6. Acetolysis of *P. ponderosa* pollen (R-4.01)

*P. ponderosa* pollen (200 mg;  $n = 3$ ) that had previously been extracted with organic solvent was suspended in 10 mL of a mixture consisting of 90% v/v acetic anhydride and 10% v/v of concentrated sulfuric acid. This suspension was stirred at  $90^\circ\text{C}$  for 15 min, then the blackened solid was collected by filtration through sintered glass. The acetolyzed pollen was washed with  $5 \times 10$  mL of glacial acetic acid,  $10 \times 10$  mL of deionized water, and  $3 \times 10$  mL of methanol, then washed with an additional  $3 \times 10$  mL of deionized water by repeated centrifugation as described previously. The solid was placed under

vacuum to yield  $118 \pm 3$  mg of putative sporopollenin as a coarse black powder. ATR-FTIR: 3394, 2928, 2857, 2646 (est), 1775 (est), 1735 (est), 1729, 1706 (est), 1645, 1605, 1515, 1488 (est), 1463 (est), 1431, 1399 (est), 1371, 1233, 1196, 1170, 1125, 1021, 946, 907, 834, 719  $\text{cm}^{-1}$ .

#### 2.2.7. Proteolysis of solvent-extracted *P. ponderosa* pollen with *Aspergillus oryzae* protease (R-2.02)

Solvent-extracted *P. ponderosa* pollen (5 mg;  $n = 3$ ) was suspended in 5 mL of 0.1 M sodium acetate buffer (pH 5.0) containing 1% w/v protease from *A. oryzae*. The suspension was heated at 40 °C for 72 h with constant agitation, then centrifuged to sediment the pollen. The pollen was subsequently washed with  $3 \times 10$  mL of deionized water by repeated centrifugation, then suspended in 5 mL of deionized water and heated at 40 °C for 72 h under constant agitation to remove any residual soluble contaminants. At the end of this incubation period, the previously described washing process was repeated with  $3 \times 10$  mL of deionized water, followed by  $3 \times 10$  mL of methanol. After evaporation of solvent under vacuum, the product was recovered as a pale yellow powder. ATR-FTIR: 3351, 3022 (est), 2926, 2855, 2737 (est), 2690 (est), 2645 (est), 1706 (est), 1679, 1630, 1605, 1589, 1551 (est), 1515, 1463 (est), 1437, 1411 (est), 1377, 1323, 1309 (est), 1283 (est), 1261, 1233 (est), 1202, 1168, 1135 (est), 1103, 1075 (est), 1038 (est), 987, 940 (est), 912 (est), 833, 775 (est), 718  $\text{cm}^{-1}$ .

#### 2.2.8. Treatment of sporopollenin with aqueous potassium hydroxide (R-1.03, R-3.02, and R-4.02)

Sporopollenin (5 mg;  $n = 3$ ) prepared by enzymatic digestion of the intine, acidolysis with phosphoric acid, or acetolysis was suspended in 5 mL of 1 M aqueous potassium hydroxide and heated at 40 °C for 72 h with constant agitation. The sporopollenin suspension was then centrifuged and the solid washed with  $3 \times 10$  mL of deionized water and  $3 \times 10$  mL of methanol by repeated centrifugation. Residual solvent was evaporated under vacuum. ATR-FTIR (enzymatic digestion; **R-1.03**): 3352, 3022 (est), 2925, 2855, 2738 (est), 2688 (est), 2618 (est), 1706 (est), 1684, 1631, 1605, 1587, 1515, 1464 (est), 1436, 1409 (est), 1379, 1347 (est), 1323, 1309, 1282 (est), 1261, 1234 (est), 1202, 1168, 1135 (est), 1103, 1051, 985, 939 (est), 832, 778, 721  $\text{cm}^{-1}$ . ATR-FTIR (acidolysis with phosphoric acid; **R-3.02**): 3370, 3021 (est), 2925, 2855, 2739 (est), 2687 (est), 2621 (est), 1702, 1682 (est), 1629, 1605, 1585 (est), 1549 (est), 1515, 1463 (est), 1437, 1409 (est), 1379, 1342, 1325 (est), 1308 (est), 1272 (est), 1243, 1202, 1169, 1137 (est), 1106, 1075, 1056 (est), 1000, 941 (est), 908 (est), 833, 773 (est), 722  $\text{cm}^{-1}$ . ATR-FTIR (acetolysis; **R-4.02**): 3363, 2924, 2857, 2643 (est), 1704 (est), 1657 (est), 1603 (est), 1565, 1514 (est), 1461 (est), 1436 (est), 1374 (est), 1170, 1096, 1035, 971 (est), 904 (est), 834, 717  $\text{cm}^{-1}$ .

#### 2.2.9. Treatment of enzymatically-isolated sporopollenin with deuterium oxide (R-1.04)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 5 mL of deuterium oxide and heated at 40 °C for 36 h. Deuterium oxide was removed and replaced with an equal volume, and the suspension was heated at 40 °C for an additional 36 h. Following this incubation period, deuterium oxide was removed under vacuum and the sporopollenin was recovered as a pale yellow powder. ATR-FTIR: 3356, 3021 (est), 2927, 2855, 1706 (est), 1680, 1631, 1605, 1588, 1552 (est), 1515, 1463 (est), 1437, 1410 (est), 1379, 1347 (est), 1324, 1283 (est), 1261, 1233 (est), 1202, 1168, 1136 (est), 1104, 985, 939 (est), 910 (est), 833, 775 (est), 720  $\text{cm}^{-1}$ .

#### 2.2.10. Treatment of enzymatically-isolated sporopollenin with methanol- $d_4$ (R-1.05 and R-1.06)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 1 mL of methanol- $d_4$  and heated at 40 °C for 72 h. The solvent was subsequently removed under vacuum and the solid was recovered as a faintly yellow powder. This procedure was repeated for an additional 72 h and the sporopollenin was ultimately recovered as a nearly colorless powder. ATR-FTIR (72 h; **R-1.05**): 3376, 3063 (est), 3014 (est), 2922, 2853, 2502, 1705 (est), 1681 (est), 1630, 1604, 1582 (est), 1556 (est), 1514, 1464 (est), 1432, 1380, 1347 (est), 1326, 1307 (est), 1283 (est), 1262, 1234 (est), 1202, 1168, 1137 (est), 1107, 982, 938 (est), 915, 833, 773 (est), 722  $\text{cm}^{-1}$ . ATR-FTIR (144 h; **R-1.06**): 3364, 3070 (est), 3030 (est), 2924, 2854, 2509, 1706 (est), 1682, 1630, 1604, 1583 (est), 1514, 1482, 1463 (est), 1435, 1408 (est), 1380, 1348 (est), 1325, 1307 (est), 1283 (est), 1261, 1234 (est), 1202, 1168, 1137 (est), 1105, 983, 938 (est), 916 (est), 833, 773 (est), 721  $\text{cm}^{-1}$ .

### 2.2.11. Treatment of enzymatically-isolated sporopollenin with sodium cyanoborohydride (R-1.07)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 5 mL of tetrahydrofuran, followed by the addition of 50 mg ( $8 \times 10^{-4}$  mol) of sodium cyanoborohydride. After 48 h at ambient temperature (20 °C), the mixture was diluted with 5 mL of deionized water and 150  $\mu$ L of 37% w/v hydrochloric acid was added. When evolution of hydrogen gas had ceased, the sporopollenin was isolated by centrifugation and washed with  $3 \times 10$  mL of deionized water and  $3 \times 10$  mL of methanol. The product was obtained as a yellow powder. ATR-FTIR: 3349, 3021 (est), 2926, 2855, 2738 (est), 2688 (est), 2623 (est), 1737 (est), 1707 (est), 1680, 1631, 1605, 1588, 1555 (est), 1515, 1463 (est), 1437, 1411 (est), 1379, 1347 (est), 1323, 1308 (est), 1282 (est), 1262, 1233 (est), 1202, 1168, 1135 (est), 1103, 985, 939 (est), 910 (est), 832, 775 (est), 721  $\text{cm}^{-1}$ .

### 2.2.12. Treatment of enzymatically-isolated sporopollenin with peracetic acid (R-1.08 and R-1.09)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 4.5 mL of deionized water, followed by the addition of 0.5 mL of 32% w/w peracetic acid solution in dilute acetic acid. This sporopollenin suspension was allowed to stand at ambient temperature (20 °C) for 72 h in the absence of light. The solid was recovered by centrifugation and was washed with  $3 \times 10$  mL of deionized water and  $3 \times 10$  mL of methanol. After evaporation of residual solvent, the product was obtained as a vivid yellow solid. The entire sequence was subsequently repeated by directly exposing sporopollenin to 0.5 mL of 32% w/w peracetic acid solution, without further dilution. After 72 h, the sporopollenin had largely dissolved and a small amount of colorless residue was recovered following the isolation procedure described above. ATR-FTIR (low conc.; **R-1.08**): 3364, 3022 (est), 2926, 2856, 2737 (est), 2689 (est), 2625 (est), 1734 (est), 1702, 1679 (est), 1632, 1605, 1588, 1515, 1464 (est), 1437, 1413 (est), 1379, 1347 (est), 1323, 1308 (est), 1279 (est), 1261, 1233 (est), 1202, 1168, 1135 (est), 1103, 1048 (est), 987, 939 (est), 833, 722  $\text{cm}^{-1}$ . ATR-FTIR (high conc.; **R-1.09**): 3371, 2944 (est), 2923, 2858, 2629, 1725, 1705 (est), 1511, 1464 (est), 1434, 1412 (est), 1374, 1323 (est), 1269 (est), 1241, 1199 (est), 1170 (est), 1150-870 (indistinct maxima), 941 (est), 844, 721  $\text{cm}^{-1}$  (est).

### 2.2.13. Treatment of enzymatically-isolated sporopollenin with elemental bromine (R-1.10)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 2.5 mL of chloroform, followed by the addition of 10  $\mu$ L ( $2 \times 10^{-4}$  mol) of elemental bromine to produce a red-orange solution. This mixture was carefully protected from light and allowed to stand at ambient temperature (20 °C) for 72 h. The chloroform was diluted with 7.5 mL of methanol, then the suspension was centrifuged to sediment the sporopollenin. The supernatant was removed and the solid was washed with  $3 \times 10$  mL of methanol by repeated centrifugation to isolate the product as a coarse tan powder. ATR-FTIR: 3411, 2930, 2857, 2645 (est), 1725, 1631, 1561, 1476, 1459 (est), 1433, 1414, 1370, 1348 (est), 1321, 1274, 1239, 1209, 1148, 1098, 1076, 1027, 873, 849, 775, 737, 714  $\text{cm}^{-1}$ .

### 2.2.14. Treatment of enzymatically-isolated sporopollenin with aqueous elemental bromine (R-1.11)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 2.5 mL of 0.1 M sodium acetate buffer (pH 5.0), followed by the addition of 100  $\mu$ L ( $2 \times 10^{-3}$  mol) of elemental bromine to produce a fuming biphasic mixture. This mixture was carefully protected from light and allowed to stand at ambient temperature (20 °C) for 72 h. Excess bromine was removed under vacuum, then the mixture was diluted with 5 mL of deionized water and centrifuged to sediment the sporopollenin. The supernatant was removed and the solid was washed with  $3 \times 10$  mL of deionized water and  $3 \times 10$  mL of methanol by repeated centrifugation. The product was obtained as a nearly colorless powder. ATR-FTIR: 3700-3100, 2929, 2856, 1736, 1462, 1437 (est), 1410 (est), 1377, 1351 (est), 1310, 1236, 1158, 1097, 1052 (est), 958 (est), 895 (est), 758, 723, 701  $\text{cm}^{-1}$ .

### 2.2.15. Treatment of enzymatically-isolated sporopollenin with acetone in the presence and absence of elemental iodine (R-1.12 and R-1.13)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 5 mL of acetone containing 0.1% w/v elemental iodine (5 mg;  $2 \times 10^{-4}$  mol). The resulting reddish-brown solution was heated at 50 °C for 72 h. To isolate the sporopollenin, the suspension was diluted with an additional 5 mL of acetone and centrifuged. The condensed solid was subsequently washed with  $3 \times 10$  mL of methanol

by repeated centrifugation and obtained as a coarse tan powder after vacuum. As a control experiment, the reaction was repeated in the absence of iodine. In this case, the solid was recovered as a pale yellow powder. ATR-FTIR (**R-1.12**): 3600–3000, 2989, 2927, 2856, 2735 (est), 2687 (est), 2638 (est), 1705, 1680, 1632, 1606, 1588, 1548 (est), 1515, 1464 (est), 1437, 1379, 1348, 1325, 1308, 1262, 1200, 1167, 1133, 1104 (est), 1020 (est), 982, 941, 874, 832, 809 (est), 777, 723  $\text{cm}^{-1}$ . ATR-FTIR (without iodine; **R-1.13**): 3362, 3021 (est), 2926, 2855, 2740 (est), 2688 (est), 2621 (est), 1705 (est), 1681, 1631, 1605, 1588, 1553, 1515, 1463 (est), 1437, 1411 (est), 1379, 1348 (est), 1323, 1308 (est), 1282 (est), 1262, 1232 (est), 1202, 1168, 1135 (est), 1103, 985, 939 (est), 910 (est), 833, 774 (est), 721  $\text{cm}^{-1}$ .

#### 2.2.16. Treatment of the sporopollenin-acetone ketal with hydrochloric acid (R-1.14)

Sporopollenin ( $n = 3$ ) that was previously derivatized as the acetone by reaction with acetone and elemental iodine was suspended in 5 mL of 6 M hydrochloric acid. This suspension was heated at 40 °C for 72 h, then the solid was isolated by centrifugation and washed with  $3 \times 10$  mL of deionized water and  $3 \times 10$  mL of methanol. An orange powder was obtained after evaporation of residual solvent under vacuum. ATR-FTIR: 3367, 3022 (est), 2926, 2855, 2738 (est), 2689 (est), 2622 (est), 1701, 1685, 1631, 1605, 1588, 1553 (est), 1515, 1463 (est), 1437, 1409 (est), 1379, 1345 (est), 1323, 1308 (est), 1282 (est), 1262, 1233 (est), 1201, 1168, 1131, 1104, 984, 941 (est), 911 (est), 868 (est), 832, 774 (est), 742 (est), 721  $\text{cm}^{-1}$ .

#### 2.2.17. Treatment of enzymatically-isolated sporopollenin with octanal in the presence of elemental iodine (R-1.15)

Enzymatically-isolated sporopollenin (5 mg;  $n = 3$ ) was suspended in 5 mL of octanal containing 0.1% w/v elemental iodine (5 mg;  $2 \times 10^{-4}$  mol) and heated at 50 °C for 72 h. The suspension was then diluted with an additional 5 mL of octanal and centrifuged to permit isolation of the sporopollenin, followed by repeated methanol washing as previously described. After evaporation of residual solvent under vacuum, the solid was obtained as a brown, amorphous material lacking distinct granularity. ATR-FTIR: 3329, 2956 (est), 2922, 2873 (est), 2854, 2732, 2678 (est), 2621 (est), 1732 (est), 1711, 1675, 1653 (est), 1631, 1606, 1587, 1554 (est), 1515, 1466, 1457, 1438, 1412, 1378, 1343, 1323 (est), 1302 (est), 1280, 1261, 1244, 1218, 1193 (est), 1139, 1116, 1058 (est), 1020, 995 (est), 983, 965, 936 (est), 879, 832, 816 (est), 773, 745 (est), 723  $\text{cm}^{-1}$ .

#### 2.2.18. Treatment of the sporopollenin-octanal acetal with elemental bromine (R-1.16)

Sporopollenin ( $n = 3$ ) that was previously derivatized as the octanal acetal was suspended in 2.5 mL of chloroform, followed by the addition of 10  $\mu\text{L}$  ( $2 \times 10^{-4}$  mol) of elemental bromine. This suspension was protected from light and allowed to stand at ambient temperature (20 °C) for 72 h. The solid was then recovered as described in the case of enzymatically-isolated sporopollenin. After vacuum, the product of this reaction was a tan residue. ATR-FTIR: 3428, 2957 (est), 2925, 2870 (est), 2855, 1730, 1631, 1561, 1483 (est), 1458, 1435, 1415, 1377, 1342, 1318 (est), 1300 (est), 1281 (est), 1265 (est), 1248, 1229, 1208 (est), 1196 (est), 1160, 1100, 1076 (est), 1059 (est), 1025 (est), 999 (est), 968 (est), 922 (est), 895 (est), 873 (est), 847 (est), 770 (est), 736, 723  $\text{cm}^{-1}$ .

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## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.dib.2020.105129>.

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