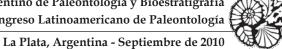
## X Congreso Argentino de Paleontología y Bioestratigrafía VII Congreso Latinoamericano de Paleontología



## Molecular characterization of a seed-fern ovule (Pennsylvanian, Sydney Coalfield, Canada) by FTIR, 13C NMR, and Py-GC-MS

J. A. D'ANGELO<sup>1</sup>, U. WERNER-ZWANZIGER<sup>2</sup>, R. HELLEUR<sup>3</sup> and E.L. ZODROW<sup>4</sup>

Despite the abundance of detached seed-fern ovules (Euramerican and Cathaysian floral provinces, Pennsylvanian-Permian) as compression / impression, their palaeobiochemistry remains unknown. The Late Pennsylvanian strata of the Sydney Coalfield, Canada, have yielded numerous ovulate trigonocarpalean compressions, 6-8cm long, with preserved cuticles assigned to Trigonocarpus grandis (Lesquereux) Cleal et Zodrow. The macerated cuticles are analyzed by Fourier Transform Infrared spectroscopy (FTIR), Carbon-13 Nuclear Magnetic Resonance (13C NMR), and Pyrolysis Gas Chromatography-mass spectrometry (Py-GC-MS). FTIR and 13C NMR data reveal a predominantly aliphatic structure including C-H groups (with or without hetero-substitution such as in alkyl and aryl alcohols, ethers, esters, and ketones). Larger CH2/CH3 ratios (above 20) suggest the presence of long and straight aliphatic side chains linked to the main macromolecular structure. Other groups present include C-O (in phenols and phenoxy structures, and aryl and alkyl ethers and alcohols), C=O carbonyl groups (in carboxylic acids and conjugated and highly conjugated structures such as ketones), C=C (in aromatic carbon structures with and without bridging to other carbon groups), and O-H (in aliphatic or aromatic alcohols). In addition, 13C NMR shows, compared to other cuticles in related seed ferns, a high amount of acetal groups as they occur in di- and polysaccharides. In agreement with FTIR and NMR results, Py-GC-MS data show the presence of highly aliphatic molecules (alkanes/alkenes) with carbons between C4 and C8 (including a complex mixture of mono and di unsaturated hydrocarbon isomers up to C8). Other compounds detected include benzene and toluene. However, the most striking chemical feature of the pyrolysates markers is the presence of 5 isomers of C5H8 including isoprene (0.5 - 1.0 % abundance). The latter could be derived from some tocopherol precursor (vitamin E-like compound). If confirmed, this is the earliest chemical evidence for the presence of isoprenoids in vascular plants.

<sup>1</sup> Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales (IANIGLA), CCT-CONICET-Mendoza, Avenida Ruiz Leal s/n, Parque Gral. San Martín, (5500) Mendoza, Argentina y Área de Química, Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Centro Universitario, (M5502JMA) Mendoza, Argentina. joseadangelo@yahoo.com

<sup>2</sup> Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada. ulrike.wernerzwanziger@gmail.com

<sup>3</sup> Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland and Labrador, Canada. rhelleur@mun.ca

<sup>4</sup> Palaeobotanical Laboratory, Cape Breton University, Sydney, Nova Scotia, Canada. Erwin Zodrow@cbu.ca