# 不同产地和不同成熟期油茶果壳木质素结构解译

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**摘 要:**【目的】对不同产地（永州、常宁、祁东和小果油茶、湘林 1 号、湘林 210）和不同成熟期（2022 年 10 月 1 日至 30 日，每隔七天采集一次湘林 53 号）油茶果壳木质素结构进行解译，为油茶果壳的高值化利用奠定基础。【方法】采用磨木木素（MWL）和双酶解木质素（DEL）为研究样品，利用 FT-IR、高效液相、热裂解气质、热重分析、核磁分析等手段对其进行全面的结构表征。【结果】从不同产地油茶果壳中提取木质素组分，结果表明油茶果壳的酸溶木质素含量较高（7.78-9.91%），六种酸溶木质素的衍生物占总木质素的 2.96-4.15%。分离的六个 DEL 样品得率较高，为 68.48-72.40%。并且具有较高纯度和均匀的化学结构，多分散性为 2.00-2.06。2D-HSQC NMR 表明，DEL 为富含愈创木酚的木质素（S/G<0.9），具有高含量的 β-O-4′芳基醚键（41.89~48.26/100 Ar）和一定数量的 C-C 键，即 β-β 连接键和 β-5 连接键。其中湘林 210 油茶壳木质素具有最高的热稳定性。从不同成熟阶段的油茶果壳中提取木质素组分，发现在油茶成熟过程中，Klason 木质素含量从 19.5%增加到 25.5%，酸溶性木质素含量由 7.4%减少到 5.9%。MWL 和 DEL 组分的分子量逐渐增加，并且 DEL 组份的多分散性随着成熟度从 2.25 逐渐降低到 1.88。CFS 木质素是 SG 型木质素，具有低 S/G 比（S/G<0.6），并含有丰富的 β-O-4′键（DEL-2 中的最大量为 58.6/100Ar）。此外，在生长过程中，MWL 和 DEL 组分中的 β-O-4′键的数量先增加后减少。五个 DEL 样品的酚类 OH 含量随着分子量的增加而从 2.05 mmol/g 逐渐降低到 1.78 mmol/g。【结论】油茶壳木质素的低 S/G 比和高 C-C 键含量表明，在通过催化解聚生产芳香族化学品方面，油茶壳木质素不是一种有竞争力的材料；然而另一方面，油茶壳木质素是开发木质素基碳材料的一种很有前途的原料。此外，油茶壳木质素优异的热稳定性表明了其在耐高温材料中的潜在应用。油茶壳木质素-碳水化合物复合物表现优异的抗氧化活性，有望升级为天然抗氧化剂。可视化结构示意图对木质纤维素材料原始木质素的结构和组成的认知极其重要，不仅有助于将生物质分解为化学成分，而且有助于了解木质素大分子在植物生长过程中的变化。因此，根据本研究确定的定量结果（如分子量、单元间键、C9 单元、S/G 比和 LC 键），提出了来自不同品种和不同成熟阶段油茶壳的原始木质素大分子的潜在结构图。

**关键词**: 油茶壳；不同产地；成熟期；结构解译

# Lignin structural elucidation of *Camellia oleifera* fruits collected from various locations and different maturity stages

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**Abstract:**【Objective】The aim of this study was to investigate the structural characteristics of lignin of *Camellia oleifera* fruit shells (CFS) from different locations (Yongzhou, Changning, Qidong and Xiaoguo, Xianglin 1, Xianglin 210) and different maturity periods (1-30 October 2022, Xianglin 53 was collected every seven days) to

lay the foundation for the high-value utilization of *Camellia oleifera* fruit shells.【Method】Milled wood lignin (MWL) and double enzymatic lignin (DEL) were used as the study samples for comprehensive structural characterization using FT-IR, high performance liquid chromatography (HPLC), thermogravimetric analysis and nuclear magnetic analysis.【Result】 The CFS from different locations had high content of ASL (7.78-9.91%), and the lignin derivatives from the six ASL account for 2.96-4.15% of CFS. The separated six DEL samples showed high yield (68.48-72.40%), high purity, and homogeneous chemical structures with the PDI of 2.00-2.06. 2D-HSQC NMR showed that the DEL were guaiacyl-rich lignins (S/G < 0.9), having high content of β-O-4 aryl ether linkages (41.89~48.26/100 Ar), and specific number of C-C linkages, namely β-β linkage (14.84-26.30/100 Ar) and β-5 linkage (9.61-13.85/100 Ar). DELXL210 had the highest thermal stability. The Klason lignin content in the CFS from different maturity periods increased from 19.5% to 25.5%, and in addition, the acid-soluble lignin content decreased from 7.4% to 5.9% during the ripening. The molecular weights of the MWL and DEL fractions gradually increased, and the polydispersity of the DEL fractions gradually decreased from 2.25 to 1.88 with maturity. The CFS lignins are SG-type lignin with low S/G ratios (S/G < 0.6), and contain an abundance of β-O-4′ linkages (maximum amount of 58.6/100Ar in DEL-2). Moreover, the amount of β-O-4′ linkages in the MWL, DEL, and LCC-AcOH fractions increased first and then decreased during growth. The phenolic OH content of the DEL fractions gradually decreased from 2.05 to 1.78 mmol/g as the molecular weight increased. 【Conclusion】The low S/G ratio and high C-C linkages content of CFS lignin indicated that CFS lignin is not a very competitive material for the production of aromatic chemicals via catalytic depolymerization; on the other hand, CFS lignin is a promising feedstock for the development of lignin-based carbon materials. In addition, the excellent thermal stability of CFS lignin hints at its potential applications in high-temperature resistant materials. The LCC-AcOH fractions exhibited high antioxidant activity, suggesting their promising upgrading into natural antioxidants. Visualizing the cognition of the structure and composition of the original lignin of lignocellulosic materials is extremely important, not only for facilitating the deconstruction of biomass into chemical components, but also for understanding the variations of lignin macromolecules during plant growth. Consequently, the potential structural diagrams of original lignin macromolecules from the CFS with different ripening stages were proposed according to the quantitative results (such as molecular weight, interunit linkages, C9 unit, S/G ratio, and LC linkages) determined in this investigation.

**Key words:** Camellia oleifera fruit shells; various locations; maturity periods; structural elucidation.