Photodegradation of natural varnishes in artworks

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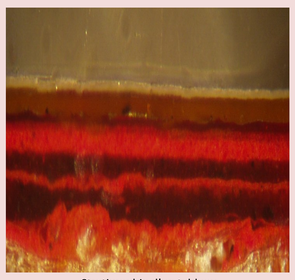
Problematic



Stratigraphie d'un tableau

Natural varnishes used in arts are generally composed of natural resins dissolved in solution. Through times those materials undergo different photochemical processes, modifying their molecular composition. Those reactions also impact the aesthetic aspect of the artwork (crackling, yellowing, etc.). In order to improve the restoration of paintings it is necessary to know the composition of those old varnishes. In this study we focused on five different diterpenic and triterpenic resins generally used in art. They are respectively mainly composed of diterpenic (abietanes, pimaranes) and triterpenic (oleanenes, ursenes, dammarenes, masticadienes) molecules.

This work aims to improve the understanding of photochemical degradation processes of natural varnishes. The multi-analytical approach enabled us to find better identification criterions of old varnishes by confronting laboratory results after artificial ageing with varnishes sampled on artworks.

Photochemical degradation under simulated irradiation

The varnishes were made following ancient recipes, diterpenic (sandarac, colophony, Manila copal) and triterpenic (mastic, dammar) resins were used with a special attention to the botanical origin. The varnishes were irradiated under artificial sunlight and analysed by GC/MS* and FTIR**.

Fresh varnishes

- **Ethanol, linseed oil or turpentine spirit**
- **Natural resin** sandarac, Manila copal, colophony (distillation product), mastic and dammar

100 µL of varnish are spread in petri dish and let to dry for 1h at $T°_{amb}$.

IRRADIATION

Aged varnishes

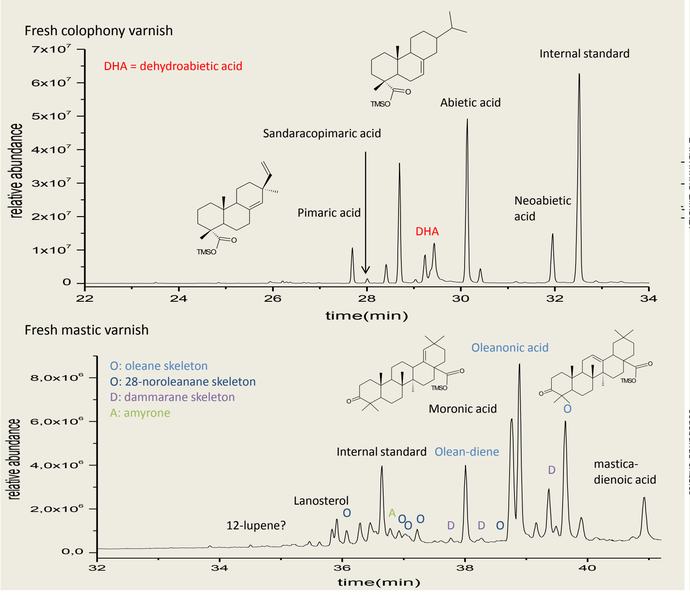
Samples are irradiated for 800h under simulated sunlight (Suntest bench, 750 $W.m^{-2}$).

Chemical analyses

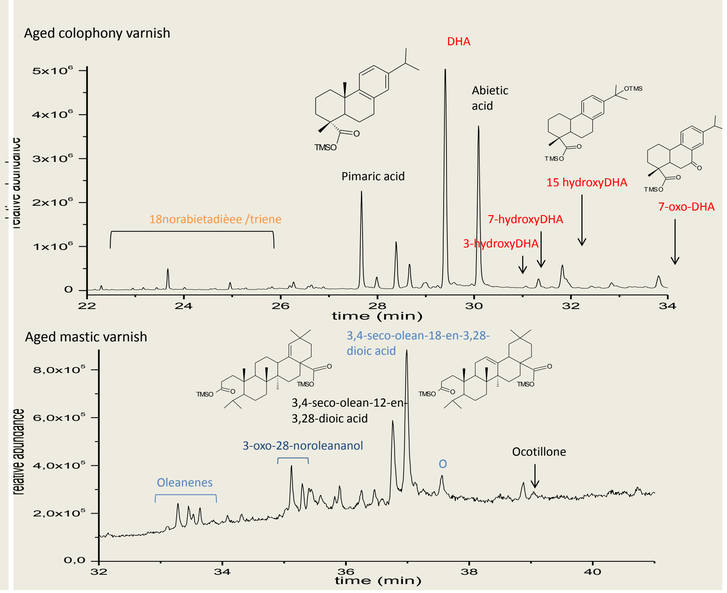
GC-MS*

The samples are extracted in dichloromethane and derivated by trimethylsilylation (BSTFA, 70°C).

Fresh varnishes

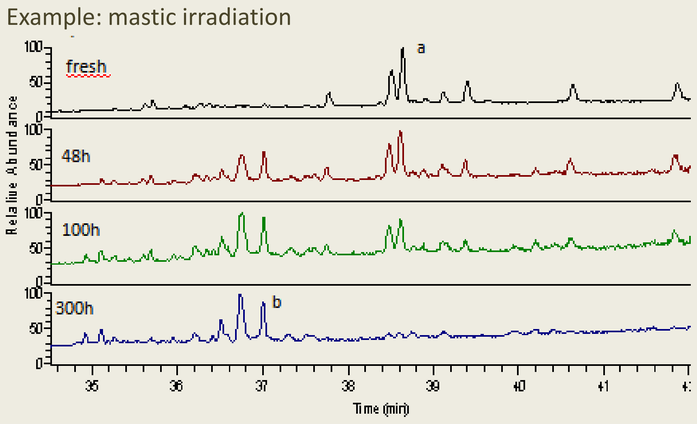


Aged varnishes

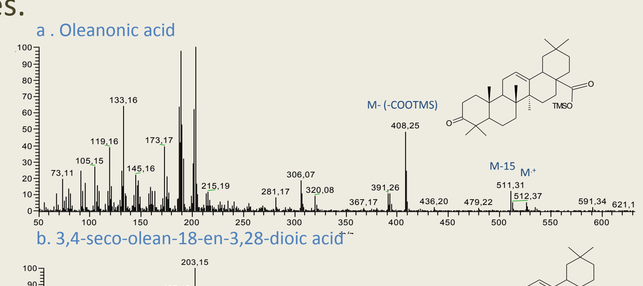


Those analyses enable to identify and characterise the chemical markers thanks to comparison with commercial standards and the development of adapted fragmentation methods in GC-MS (variation of the ionization energy, MS/MS). During irradiation various hydroxylated compounds appear giving information on the aging of varnishes.

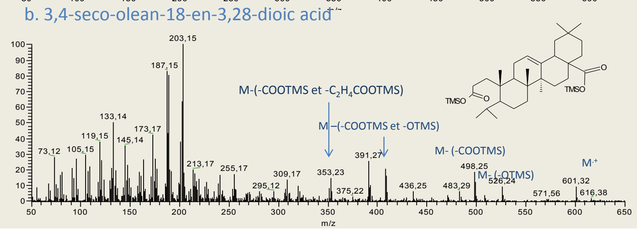
Example: mastic irradiation



a . Oleanonic acid

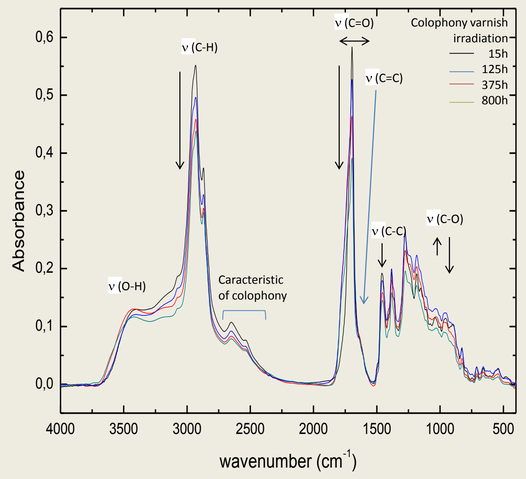


b. 3,4-seco-olean-18-en-3,28-dioic acid



FTIR**

KBr pellets are coated with the varnish and then irradiated. The pellets were periodically analysed by FTIR to follow the photodegradation process.



The irradiations enable to highlight the two major degradation processes:

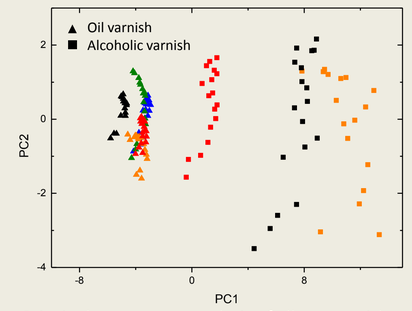
- Oxidation process: augmentation of the absorbance of the C-O (800-1330 cm^{-1}) band and widening of the carbonyl band (1700-25 cm^{-1}).
- Double bonds reactivity: C=C (1645 cm^{-1}) and C-H (2890-3025 cm^{-1}) bands decrease.

Identification of varnishes

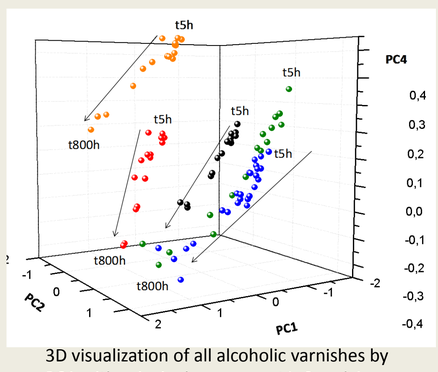
<u>Fresh varnishes</u>: Characteristic bands for varnishes were found. They enable to identify the different diterpenic and triterpenic varnishes.

<u>Aged varnishes:</u> Many characteristic bands disappear with ageing. Yet we can still differentiate diterpenic and triterpenic resins in the case of alcoholic and spirit varnishes.

Principal component analysis was performed to improve the identification. This way we could separate our oil varnishes and observe the loss of variance in the different spectra with ageing.



Principal component analysis of all our varnishes

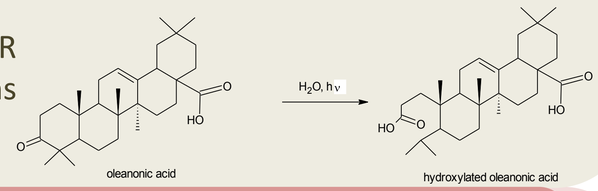


3D visualization of all alcoholic varnishes by PCA with principal component1, 2 and 4 .

Major degradation mechanisms

For colophony, the photochemical reactions lead to the aromatisation of an abietic acid cycle forming dehydroabietic acid (DHA). FTIR and GC-MS results show that the hydratation reactions provoke the apparition of hydroxylated abietanes. These hydratation reactions also occur in triterpenic varnishes whose one of the major compounds is oleanene molecules.

Ex : hydratation of oleanonic acid



oleanonic acid — hydroxylated oleanonic acid

Identification of ancient varnishes

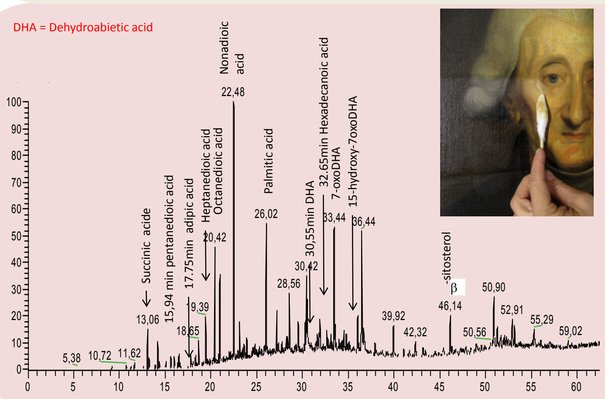


Photo credits: « Portrait du Baron Portal », Fabre Museum, Montpellier- © I.Devergne

Thanks to collaborations with professional restorers we collected various samples of ancient artwork varnishes. Those are most of times more complex than the varnishes we made as they an have different resins mixed. Chemical markers enabled to identify the type of varnish and the resins used.

The chemical compositions were compared to the data base we made in the first part of this work. A large number of the identified molecules (DHA, 7-oxoDHA, 15-hydroxyDHA) were present in our experimental varnishes after artificial ageing (cf. figure on the left). It lead to the determination of an oil varnish with colophony. The chemical markers confirm the fundamental role played by the light in the degradation process and the validity of our experimental protocol.

*Gas Chromatography coupled with Mass Spectrometry ** Fourier Transform InfraRed spectroscopy