Advanced diagnostics and characterization of vegetable and synthetic tannins: the holistic approach.

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▪ Introduction

Natural polyphenols represent tanning agents known since ancient times, and in the last decades have inspired the synthesis of many synthetic tannins and their marketing. Vegetable tannins are polyphenols with optimum tanning properties with high molecular weight, that are produced in roots of woody, woods, leaves and plants galls. Vegetable tannings main traditional use is the production of sole leather for high quality shoes, leather goods, harnesses and to produce leather for automotive industries and as retanning agents for many other articles. At the best of our knowledge, no standardized analytical methods is known for the identification and analysis of the constituents of mixtures of vegetable and synthetic tannins.

Aim of the work

In this work vegetable and synthetic tannins have been characterised by several techniques. The aim of this study is firstly to extract and characterize various type of tannin (commercial product) and then to perform analysis by high-performance techniques.
At this regards, tannins agents were characterized by evaluating of the moisture and ashes, pH of analytical solution, heavy metals and metals by inductively coupled plasma with mass spectrometry, HPLC-UV. HPLC-MS/MS was used to perform qualitative-quantitative analysis, while structural investigations were performed by
^{1}H-NMR and ^{13}C NMR experiments, and Fourier Transform Mass Spectrometry (HR-FTICR) by using the SolariX XR Hybrid Fourier Transform Mass Spectrometer 7T.

▪ Gravimetric analysis of vegetable and synthetic tannins

Tannins	Moisture	Ashes 550 °C	Ashes 800 °C	pH
Chestnut	8,2 %	1,3%	1,4 %	3,6
Gambier	7,6%	25,8%	25,0%	4,6
Mimosa	6,6%	3,6%	2,9%	5,3
Quebracho	7,8%	7,6%	7,3%	5,1
Tare	7,5%	4,7%	3,4%	3,5
DPS powder	3,8%	41,0%	40,9%	4,8
DPS conc.	6,0%	40,7%	40,1%	4,5
Phenolic	3,8%	40,5%	40,4%	4,4
Naphthalene	56,0%	11,6%	11,4%	6,9

The pH value was measured of the analytical solution prepared according to UNI EN ISO 14088:2020 standard (analytical solution 4 g / L)

▪ Metals determination by ICP-MS

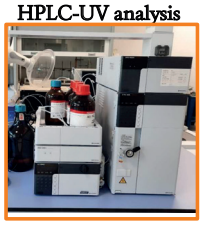
Tannins	Chestnut	Gambier	Mimosa	Quebracho	Tare	DPS powder	DPS conc.	Phenolic	Naphthalene
Cr(mg/Kg)	< LOQ	2.7	< LOQ	< LOQ	2.0	1.0	< LOQ	< LOQ	< LOQ
Al (mg/Kg)	195.0	6157.8	134.6	42.4	292.4	133.9	18.3	171.5	6.6
Fe (mg/Kg)	< LOQ	983.5	75.6	< LOQ	< LOQ	50.8	45.9	44.9	9.8
Ti (mg/Kg)	< LOQ	365.1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Zr (mg/Kg)	< LOQ	18.34	8.8	< LOQ	0.9	9.8	10.3	11.0	2.3
Na (mg/Kg)	1687.8	3586.2	1155.2	16245.5	367.5	95324	104530.9	102202.4	35187.4
K (mg/Kg)	1736.2	3611.9	5707.3	816.5	12522.2	448.7	578.8	496.5	832.1
Mg (mg/Kg)	942.4	471.6	949.9	859.6	325.7	112.4	8.2	85.7	27.2
Ca (mg/Kg)	774.2	14779.8	1362.5	3556.9	1526.8	1034.1	779.5	758.7	207.0
Si (mg/Kg)	1070.0	28729.3	3723.9	7422.7	3267.8	4904.4	5237.3	6219.3	1486.9

▪ Characterization of bisphenols

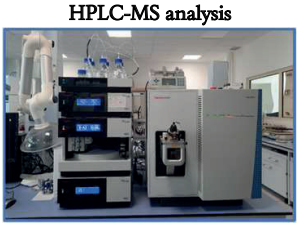
Extraction



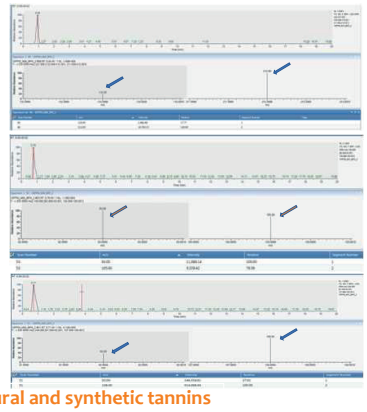
HPLC-UV analysis

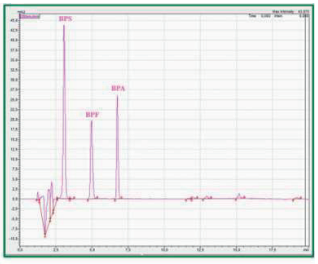


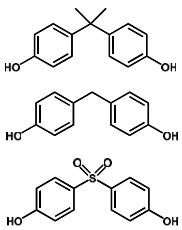
HPLC-MS analysis



Instruments with high sensitivity and low detection limits were used for the analysis of these substances, in particular high performance liquid chromatography coupled with UV detector (HPLC-UV) and high-performance liquid chromatography coupled with MS detector (HPLC- MS).







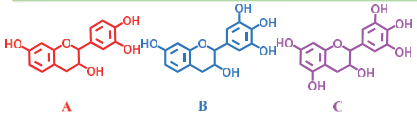
Bisphenol A m/z: 133 - 212

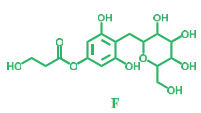
Bisphenol F m/z: 93 - 105

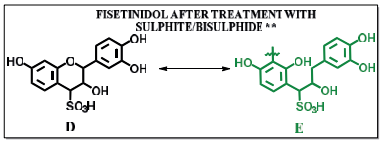
Bisphenol S m/z: 92 - 108

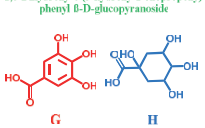
No evidence of BPA in the analyzed samples but some positive values of BPS in natural and synthetic tannins

▪ Characterization by ESI(-) - FTICR









Tare

Compounds	m/z
HG	343.06721
HGG	495.07824
HGGG	647.08944
HGGGG	799.10064
HGGGGG	951.11174
HGGGGGG	1103.12318
F	375.09327
FG	527.10463
FGG	679.11568
FGGG	831.12743
FGGGG	983.13862
FGGGGG	1135.15039

Chestnut

Compounds	m/z
Ellagic Acid	300.99916
1-O-Galloyl-β-D-glucose	331.06730
Geshoidin	377.08805
Castalagin	466.02881 933.06578
di-O-galloyl- β -D-glucose	483.07857
Grandinin	532.04994 1065.11082
Castacrenin D	542.03440 1085.07794
Castacrenin (A-B-C)	613.04798
tri-O-galloyl- β -D-glucose	635.08986
Fusicoccin*	679.37084
tetra-O-galloyl- β -D-glucose	787.10156

Quebracho

Compounds	m/z
AB	561.14273
AAB	833.21429
AAAB	1105.28617
D	353.03473
EB	643.11609
EAB	915.18762
EAAB	1187.26069
EAAAB	729.16010
EAAAAB	874.20132
EAAAAAB	1010.23616
Ellagic acid diglucoside	625.10562

Mimosa

Compounds	m/z
B	289.07234
BB	577.13772
BBA	849.20860
AB	561.14259
CB	593.13272
CAB	865.20421

* Fusicoccin is produced by several plant fungal infections.
** Several commercial extracts are often sulfited to reduce their viscosity and increase their solubility in water

▪ Conclusion

The activity was carried out as a preliminary study for the development of analytical methods on samples of chemical products but also on wastewater.
The values of the metals are, in some cases (confirmed by ashes value), high : being commercial samples, the characteristics detected may depend on the blend developed by the distributor, rather than an intrinsic characteristic of the tannin.
The need to develop an analytical method for bisphenols arises from their inclusion in SVHCs. Using HPLC-UV we can obtain a rapid result that can be confirmed by HPLC-MS. New methods can provide a direct and rapid method using only HPLC-MS.
HR-FTICR analysis shows different composition for the natural tannins. Quebracho and mimosa show a similar polyflavonoid composition while the Tare sample is formed by oligomeric mixtures of gallic acid and quinic acid.