

Highlights of Analytical Chemistry in Switzerland

Division of Analytical Chemistry

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Identification of a Red Wine Marker in Residues from a 13th Century Cellar

David Drissner^{*a}, Peter Gehrig^b, Reto Marti^c, Erwin Hildbrand^d, and Frank Hesford^a

^{*}Correspondence: Dr. D. Drissner^a, Tel.: +41 44 783 64 29, Fax: +41 44 783 62 24, E-Mail: david.drissner@acw.admin.ch

^aAgroscope Changins-Wädenswil Research Station ACW, Food Microbiology & Special Analytics, Schloss, CH-8820 Wädenswil; ^bFunctional Genomics Center Zurich, University of Zurich and ETH Zurich, Winterthurerstrasse 190, CH-8057 Zurich; ^cArchäologie Baselland, Amtshausgasse 7, CH-4410 Liestal; ^dThe Swiss National Museums, Collections Centre, Lindenmoosstrasse 1, CH-8910 Affoltern a. Albis

Keywords: MALDI-TOF/TOF · Matrix-Assisted Laser Desorption/Ionisation-Time Of Flight/Time Of Flight mass spectrometry · Oenological history · Red wine marker · Syringic acid

In 2007, archaeologists of the canton Baselland discovered the remains of a building from the late 13th century in Pratteln. These buildings were part of the medieval Meier yard (Latin: *maior*, local bailiff) belonging to the monastery St. Alban in Basel founded in 1083. Castings of timber beams in the floor of one cellar have been interpreted as supports for wine barrels. Puzzling red-brownish colorations in the floor of the neighboring cellar were postulated to be caused by red wine and to indicate the location of the wine press, respectively. To test this, we applied the highly specific and sensitive technique of MALDI-TOF/TOF

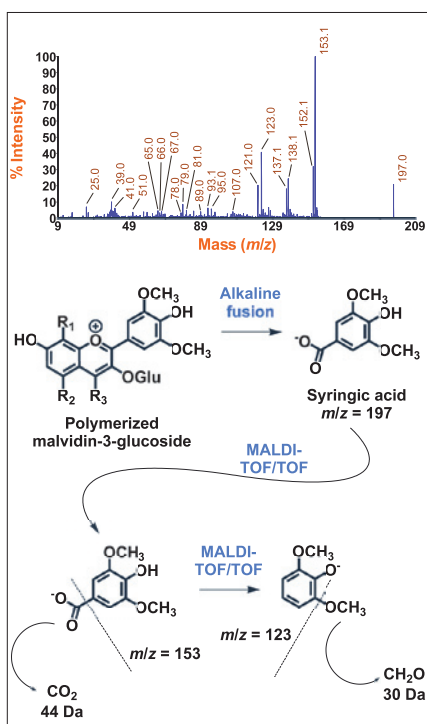
mass spectrometry for the first time to screen for the red wine marker syringic acid in the colored floor samples.

Upon ageing, malvidin-3-glucoside, a major natural pigment in red wine, polymerizes to complex, stable, red-brownish pigments. Alkaline fusion releases syringic acid from the malvidin-3-glucoside present in these complex pigments. Analyses of prepared samples were performed with an Applied Biosystems 4800 MALDI-TOF/TOF Analyzer in the negative-ion mode using 3-aminoquinoline as the matrix.

We detected a specific signal with $m/z = 197$ (corresponding to deprotonated syringic acid) in the colored floor sample. This signal was absent in controls from non-colored sites of the floor. Collision-induced dissociation of that precursor ion resulted in prominent fragment ions with $m/z = 153$ and 123 , which could be explained by the loss of CO_2 (44 Da) and of CH_2O (30 Da) molecules from the molecular ion. Comparison of the fragmentation pattern with that of a syringic acid reference finally proved the presence of syringic acid in the colored samples. The identification of syringic acid thus revealed the red wine origin of the preserved, colored residues in the medieval cellar.

In support of historical records, these results provide the first proof by analytical chemistry that red wine was produced already in the 13th century in Pratteln. In this study, MALDI-TOF/TOF mass spectrometry helped to identify the ancient Meier yard as a wine farmhouse and is proof of one of the oldest medieval wine farmhouses in Switzerland. This application of a MALDI-TOF/TOF instrument has helped to unravel oenological history in Switzerland, and it is also a promising tool for future applications in food sciences.

Received: January 8, 2009



MALDI-TOF/TOF spectrum of syringic acid in the colored sample (top). Release of syringic acid from malvidin-3-glucoside through alkaline fusion and subsequent analysis by MALDI-TOF/TOF MS. The structures of malvidin-3-glucoside in the polymerized pigment, syringic acid, and the two fragment ions with $m/z = 153$ and 123 , respectively, are shown (bottom).



Red-brownish colorations in the floor of the medieval cellar (Picture: Archäologie Baselland)

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Please contact: Dr. Veronika R. Meyer, EMPA St.Gallen, Lerchenfeldstrasse 5, 9014 St.Gallen
Phone: 071 274 77 87, Fax: 071 274 77 88, Mail to: veronika.meyer@empa.ch