APP11-P10-We - Quantitative determination of stilbenoids and proanthocyanidins on a C18-Core shell column in series with DAD and fluorescence detection and LC-MS/MS identification

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Grape canes, the annual pruning residue of vines, contain interesting levels of (*E*)-resveratrol and of oligomeric stilbenoids, together with proanthocyanidins [1, 2]. To quantify these two types of (poly)phenolic compounds in grape canes and in extracts derived from them in one chromatographic run, only with UV detection is complex, due to analytical interferences between both types of (poly)phenolic compounds and due to a comparatively low UV-absortivity of some procyanidins. These limitations can be overcome by replacing a conventional C-18 column by a core-shell column and combining in series a DAD-UV-detector and a fluorescence detector. For separation and identity assignation of procyanidins, prodelphinidins and stilbenoids (monomers to tetramers) in a grape cane extract by LC-DAD-FL-MS/MS was used a 0.1 % formic acid and 30: 70 (v/v water/acetonitrile) as mobile phases A and B, respectively, on gradient at mobile phase flow rate of 0.4 mL/min on a C-18 core shell column 250 x 4.6 mm, 2.7 micrometer particles at 30 °C. Under these conditions, a good separation of proanthocyanidins and oligostilbenoids is achieved, even if one run takes around 60 min. For a faster and efficient analysis, a quantitative HPLC-DAD-FL method was developed, using the same column without loosing much efficiency, raising the flow rate from 0,4 to 1.4 ml/min, with the consequent pressure increment (1300 psi to 5400 psi). By this way, it is possible to quantify in 22 min monomeric, dimeric and trimeric procyanidins, monogallate dimers, *E*-resveratrol and oligostilbenoids. For ampelopsin A, the detection limit is improved with fluorescence detection (LOD: 0.53 mg/L), in comparison with DAD-UV detection (LOD: 0.98 mg/L).

Finally, grape canes of Cabernet Sauvignon and Pinot Noir were analyzed by the proposed method. Canes were stored under controlled conditions immediately after pruning at 30°C and 70% relative humidity and sampled successively at different increasing storage periods (0 to 14 weeks). (*E*)-resveratrol and (*E*)-piceatannol content increased after 14 weeks, while (*E*)-ε-viniferin and ampelopsin A do not have this great concentration increases. These results are according to [3]. The proanthocyanidin profile shows minor variations during storage, (-) epicatechin and B1 decreased their concentrations.

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References:

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