In this study the characterization of white wines produced from the monovarietal 'Greco bianco' grape variety is presented for the first time. A total of 40 commercial wines, from two different southern Italian regions, Calabria and Campania, from the same grape variety and two different vintages, were investigated. The analyses were performed by means of chromatographic methods, conventional analyses, and nuclear magnetic resonance (NMR) spectroscopy. No differentiation was observed according to the year of production but a significant discrimination was achieved using principal component analysis (PCA) and partial least squares-discriminant analysis (PLS-DA). In particular, PLS-DA allowed the selection of compounds (total acidity; citric, malic, succinic, and lactic acids; total polyphenol index; glucose and proline/arginine ratio) useful for differentiating the studied wines on the basis of geographical origin.