Supercritical Fluid Extraction of Eucalyptus Volatile Oil in View of Thermodynamic Modelling.

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The extraction with supercritical carbon dioxide (scCO2) is very well suited for obtaining plant extracts rich in essential oils of authentic composition. The main components of essential oil are usually terpenoids: monoterpenes, oxygenated monoterpenes, sesquiterpenes, and oxygenated sesquiterpenes. It is well known that the solubility of these substances in scCO2 decreases with increasing molecular size and number of hydroxyl groups in a molecule. Thus, under mild extraction conditions, the mixture of terpenoids in extract is initially richer in the most soluble monoterpenes and contains almost no sesquiterpenes, and only gradually the mixture composition approaches that which was originally in the plant and which can be determined by extraction with n-hexane. In contrast to *n*-hexane, $scCO_2$ does not leave any traces of foreign substances in extracts, which can be directly used in various cosmetic or food products. Evidently, a good knowledge of the relationship between the composition of the mixture in the plant and solubility of its components in scCO2 under different pressures and temperature would enable standardization of plant extracts by the control of extraction conditions.

The aim of this contribution is to determine this relationship in the case of eucalyptus oil. The oil from the leaves of *Eucalyptus grandis* L., which was selected for experiments, is rich in a monoterpene α-pinene, a monoterpene oxide 1,8-cineole, a sesquiterpene aromadendrene, and a sesquiterpene alcohol globulol. The composition of saturated vapour phase in volatile oil+CO_2 system was measured by sampling the extract from either milled dry leaves or essential oil on inert carrier, using a sufficiently large solvent residence time. Gas chromatography was used to analyse the composition of the samples, leaves, and essential oil. The extraction pressure and temperature were varied in the region of $scCO_2$ with relatively low density, where the solvent selectivity is more pronounced. The experimental results were used to determine the temperature dependence of the parameters of thermodynamic model for the studied system.

Finally, the calculation of mixture solubility in $scCO_2$ based on thermodynamic modelling was implemented in a model for extraction kinetics, and optimum extraction conditions were calculated for several examples of eucalyptus leaves composition where a fixed composition of CO_2 extract is the optimization criterion.