



## Natural oxidation of monoterpenes in *Protium heptaphyllum* oilresin

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*Protium heptaphyllum* (Burseraceae) produce an oilresin rich in volatile and non-volatile terpenes which has cosmetic and medicinal application. The oilresin texture changes as it ages, ranging from a semi-solid to a solid texture. The aim of this present work was to evaluate whether this aging process affects the volatile composition of the oilresin. Oilresins were periodically collected in São João da Barra, State of Rio de Janeiro, during the years 2013 and 2014. They were characterized by their texture: the oilresins of recent exudation (ORE) had semi-solid texture, while the oilresins of late exudation (OLE) had solid texture. Mixtures (MO) of ORE and OLE have also been collected. The oilresins (n=20) were hydrodistilled with a Clevenger apparatus for 4 hours. The essential oils (EOs) obtained were analyzed by GC/FID and GC/MS, using Agilent system 5973N, with a capillary column HP-5 (30mX0.25mmX0.25µm). The temperature was programmed from 60 to 240°C (3°C/min). The identification was made by comparison of the mass spectra (Wiley database) and retention indices calculated from the injection a series of n-alkanes. The major constituents of EOs were  $\alpha$ -pinene (3.6-19.4%), *p*-cymene (4.3-43.0%), limonene (5.8-11.6%), terpinolene (8.8-69.7%) and *p*-cymen-8-ol (2.7-31.8%). Though there were differences in the content of EOs directly related with the collection time, we found that the percentage content of *p*-cymene, terpinolene and *p*-cymen-8-ol was highly depending on the aging stage of the oilresin. The EOs obtained from ORE (n=10) were mainly constituted of terpinolene (28.2-69.7%), whereas the EOs obtained from OLE (n=8) were mainly constituted of *p*-cymene (18.7-43.0%) and *p*-cymen-8-ol (8.2-31.8%). The percentage contents of *p*-cymene and *p*-cymen-8-ol in the EOs obtained from ORE were 4.3-23.3% and 2.7-9.8% respectively, while the content of terpinolene in the EOs obtained from OLE was 8.8-20.9%. Also, the MO (n=2) presented increased percentages of terpinolene (16.3-35.5%) and *p*-cymene (19.8-29.9%), and a content of *p*-cymen-8-ol (11.1-14.6%) in-between the ranges found for these components in semi-solid and solid oilresins. These results bring strong evidence that terpinolene could be oxidated into *p*-cymene, and then *p*-cymene into *p*-cymen-8-ol (Figure 1) as a natural aging process.

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