Chemical Profile of Flower Hop Essential Oils and its Chemometric Classifications

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The Hops (*Humulus lupulus* L.) belongs to the botanical family Cannabaceae and plays an important role in the brewing industry history, giving the product durability, characteristic odor and bitterness (1). It can be said that these features occur due to high levels of essential oils and resins existing in its flowers (2). Despite its importance, essential oils belonging to this plant are poorly studied (3). The plant material was obtained commercially in Pato Branco - PR and after dried and ground, the essential oil has been obtained through hydrodistillation using a Clevenger apparatus. The extraction was done in triplicate using 30 g for each sample. The extraction time was 4 h and the essential oil was collected using diethyl ether, and dried with anhydrous sodium sulfate. Each essential oil sample was stored in vials and kept refrigerated until analysis, which was done using a GC-431 gas chromatograph associated with a MS-210 mass spectrometer, both of Varian® brand. One microliter of each sample was injected in the gas chromatograph at 250 °C, with a column flow of 1.2 ml min^{-1}. The column temperature ranged from 50 to 240 °C. The initial temperature during first minute was of 50 °C, the slope used corresponded to a 3°C min^{-1} over the following 3 min, and 3.5 °C for the remainder of the analysis. The final temperature was maintained unchanged for 14.5 min resulting in a total analysis time of 70 min. The identification of hop essential oil constituents was based on retention indexes (4), obtained by co-injection of a mixture of *n*-alkanes standards, and by comparison of their mass spectra. The results were classified by the principal coordinates analysis (PCoA), for this purpose the software PAST was used (5). Specific compounds were selected from the resulting chromatograms and an average of 63.1 % were identified among all three assays. It was observed that among the 45 compounds identified in the three hop flower samples, 12 compounds were present in all of them, namely: *p*-methyl-acetophenone (0.7 %), verbenone (0.4 %), carvacrol methyl ether (0.4 %), perilla aldehyde (0.3 %), 2,3,4-trimethyl-benzaldehyde (0.9 %), α-humulene (2.2 %), cadina-1-(6)-*trans*-4-diene (5.9 %), β-selinene (10.5 %), α-selinene (6.1 %), δ-amorphene (5.1 %), *trans*-calamenene (3.3 %) and selina-3,11-dien-6-α-ol (4.8 %). The main compounds among the samples were *epi*-α-muurolol (29.9 %), humulene epoxide II (28.6 %), β-selinene (10.5 %), 1-epi-cubenol (9.0 %) and *allo*-aromadendrene epoxide (7.7 %). The principal component analysis showed lack of uniformity among the assays.

1. Bernotienė, G.; Nivinskienė, O.; Butkienė, R; Mockutė, D. Chemija, 2004, **15**, 31-36.
2. Farag, M.A.; Wessjohan, L.A. J. Adv. Res., 2013, **4**, 417-421.
3. Sharpe, B. F. R.; Laws, D. R. J. J. Inst. Brew., 1981, **87**, 96-107.
4. Adams, R.P. Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry. 4.ed. Illinois: Allured Publishing Corporation, 2007.
5. Hammer, Ø.; Harper, D.A.T.; Ryan, P.D. Palaeontol. Electron., 2001, **4**, 4.

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