

PP66. Chemical composition of the essential oil from the aboveground parts of *Santolina chamaecyparissus* L. from Greece: NMR determination of the exocyclic double bond geometry of the major spiroketal-enol ether polyynic constituent

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Santolina chamaecyparissus L. (Asteraceae), commonly referred to as cotton lavender, is a semi-woody perennial plant with aromatic evergreen foliage, native to the Mediterranean area. Thus far, a number of researchers have analyzed the composition of the essential oil of this plant taxon, and these studies reveal a great variation in the content and identity of its volatile secondary metabolites. Herein we present a detailed GC-MS analysis of the essential oil obtained by hydrodistillation from the fresh aboveground parts of *S. chamaecyparissus* collected during winter time in Greece (central Macedonia). Fifty-four constituents were successfully identified from the small amount (0.325% yield) of the dark yellow essential oil, representing almost 97% of the total detected GC-peak areas. The main constituents of the essential oil were found to be artemisia ketone, vulgarone B, and 7-(2,4-hexadiynylidene)-1,6-dioxaspiro[4.4]nona-2,8-diene. The mass spectrum of the detected spiroketal-enol ether polyynic, along with an extensive literature research of RI values were not sufficiently informative to infer the exocyclic double bond geometry of this major constituent of the essential oil. However, a direct analysis of ¹H- and ¹³C-NMR spectra (recorded at 400 MHz, in CDCl₃) of the essential oil combined with 2D NMR experiments (gradient ¹H-¹H COSY, HMBC, and HSQC) enabled the full structural and stereochemical assignment. Additionally, the chemical shift of the enol ether proton (on the very double bond) was in an agreement with literature data [1] and we concluded that the compound in question was (*Z*)-7-(2,4-hexadiynylidene)-1,6-dioxaspiro[4.4]nona-2,8-diene. The comparison of mass spectra of the *Z*- and *E*- isomers (the latter was present in the oil with 0.85%) shows minor differences, which strongly indicates that the mass spectra alone would not be adequate for a reliable identification.

References:

[1] Bohlmann, F. et al., 1963. Tetrahedron Lett. 4, 1605–1610.

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