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ISOORIENTIN 7,3'-DIMETHYL ETHER, A NEW *C*-GLYCOSYLFLAVONE FROM *ACHILLEA CRETICA*

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Within the genus *Achillea*, the accumulation of *C*-glycosylflavones is an important chemotaxonomic character [1, 2]. *A. cretica* L., a member of section *Santolinoidea*, is characterized by the predominance of 6-*C*-glucosylflavones: isoorientin, isoorientin 7-*O*-methyl ether (swertiajaponin), isovitexin 7-*O*-methyl ether (swertisin), besides some di-*C*-glycosylflavones in the leaf extract [1]. A new *C*-glycosylflavone was obtained as a byproduct during the isolation procedure. Its UV spectrum (243, 254 sh, 271, 345 nm) was of the luteolin type; the $AlCl_3$ and $AlCl_3$+HCl shifts showed the presence of free 5-OH and the absence of free *o*-dihydroxy groups; the large bathochromic and hyperchromic effects of NaOMe on band I (406 nm) characterized a free 4'-OH group confirmed by NaOAc (408 nm), but the lack of any shift of band II with the latter showed substitution at the 7-OH group [3]. The chromatographic properties of the compound and co-occurrence with isoorientin and isovitexin 7-*O*-methyl ethers in the same extract suggested a 7,3'-di-*O*-methyl substitution, which was confirmed by the MS of the perdeuteriomethyl (PDM) derivative. The molecular peak *m/e* 578 and the base peak (M-184) agreed with a PDM *C*-hexosyl di-*O*-methylluteolin and the M-18 and M-34 peaks showed the *C*-hexosyl group to be in the 6-position [4]. The β-D-glucopyranosyl structure of the *C*-hexosyl group was deduced from TLC comparison of the permethyl (PM) derivative of the new compound with authentic PM isoorientin which showed complete identity in conditions where PM *C*-β-D-glucopyranosides and *C*-β-D-galactopyranosides are separated [5].

Thus the compound is isoorientin 7,3'-di-*O*-methyl ether (6-*C*-β-D-glucopyranosyl-5,4'-dihydroxy-7,3'dimethoxyflavone), an as yet undescribed *C*-glycosylflavone. Chromatographic surveys showed this new compound to be of restricted distribution within the genus *Achillea* and the available amount precluded further characterization.

EXPERIMENTAL

Dried leaf tissue from *A. cretica* (collected in Crete from natural habitat) was thoroughly extracted with 70% EtOH and the aq. residue was chromatographed on a Whatman CF 11 cellulose powder column eluted with H_2O. The glycosidic fractions were purified by preparative PC (Whatman 3MM) in BAW (4:1:5), $CHCl_3$–HOAc (1:1, water saturated) (CAW) and 15% HOAc. UV spectra were recorded using standard procedures [3], MS 70 eV. Perdeuteriomethylation and permethylation were carried out using the method previously described [4]. The voucher specimen is deposited at the Herbarium WU (Institute for Botany, University of Vienna).

UV λ_{max} nm: 345, 271, 254 sh, 243 (MeOH); 385, 367 sh, 297 sh, 280, 266 sh ($AlCl_3$); 380 sh, 356, 295 sh, 279, 260 sh ($AlCl_3$+HCl); 406, 300 sh, 268 (NaOMe); 408, 365 sh, 268, 255 sh (NaOAc); 347, 270, 255 sh, 242 sh (NaOAc+H_3BO_3). TLC $R_f \times 100$, Cellulose: 59 (BAW), 82 (CAW), 36 (15% HOAc). Si gel, permethyl ether ($CHCl_3$–EtOAc–Me_2CO, 5:4:1): 0.28. MS *m/e* (%), PDM ether: M^+ 578 (18), M-18 (13), M-34 (46), M-52 (9), M-109 (13), M-170 (13), M-173 (13), M-184 (100), M-201 (22), 347 (13), 203 (22), 185 (24), 168 (18).

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