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ESSENTIAL OILS OF FIVE *TANACETUM VULGARE* GENOTYPES

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Key Word Index—*Tanacetum vulgare*; Compositae; genotypes; essential oils; terpenes; γ-campholenol; 4-thujen-2α-yl acetate; chemical variation; spectral data.

Abstract—The essential oils of five *Tanacetum vulgare* genotypes were investigated and their main components identified. Artemisia alcohol, γ-campholenol, davanone, lyratol, lyratyl acetate and 4-thujen-2α-yl acetate have not been reported before as constituents of *Tanacetum vulgare*. This is the first time that γ-campholenol has been isolated from a natural source. 4-Thujen-2α-yl acetate is a novel compound.

INTRODUCTION

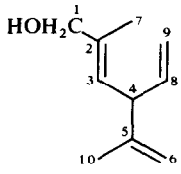
A few years ago two of us (E.H. and P.T.) described differences within *Tanacetum vulgare* genotypes growing in Hungary with regard to their essential oil content and composition [1]. We have now investigated the essential oils of three new genotypes and further characterized the oils of two of those (Nos. 403, 422) previously reported. The oils were obtained in the autumn of 1979 from plants grown in the botanical garden of the Research Institute for Medicinal Plants in Budakalász, Hungary [2].

RESULTS AND DISCUSSION

The five oils, numbered 403, 409, 422, 448 and 469, were analysed by GC/MS. Where necessary, unknown compounds were isolated by preparative GC, and identified by comparing their spectra with those of authentic samples or with spectra reported in the literature.

Oil No. 403 ($[\alpha]_D^{20.5}$ +11.8°) contained five main components which were identified as thujone (18%), borneol (16.5%), bornyl acetate (6.5%), lyratol (**1**, 26.5%) and lyratyl acetate (28%) [3–5]. Oil No. 409 ($[\alpha]_D^{20.5}$ +35.9°) contained two major components making up 75% and 18% of the total respectively. The spectra of the main component were identical with those of *trans*-chrysanthenyl acetate [6]. The second component (18% of the oil, M^+ 152) was shown to be *trans*-chrysanthenol. Hydrolysis of *trans*-chrysanthenyl acetate gave an alcohol, of which the MS and also GC retention times were identical with those of the second component. This genotype of *Tanacetum vulgare* L. occurs frequently in Hungary. Variations in the amounts of the two components are genetically determined and characteristic of the particular region of occurrence.

The two main components of oil No. 422 ($[\alpha]_D^{20.5}$ −103.5°) were both acetates (M^+ 194). One (25% of the oil) was identical with *trans*-carveyl acetate. The other (40% of the oil) was a novel compound and identified as 4-thujen-2α-yl acetate (**2**). The alcohol fragment of this acetate has an M^+ 152. The ^1H NMR shows 18 protons, three methyl groups (the acetate methyl and an isopropyl group) and only one double bond (an exocyclic methylene, confirmed by IR (Fig. 2) and ^{13}C NMR). This indicates the presence of two rings. The ^{13}C NMR spectrum shows, in addition to the acetate signals, two



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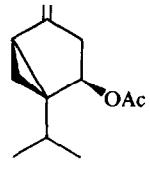

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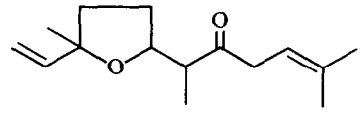

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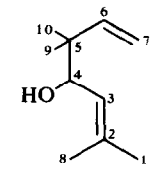

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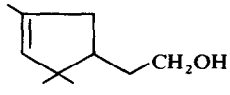

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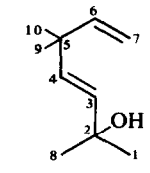

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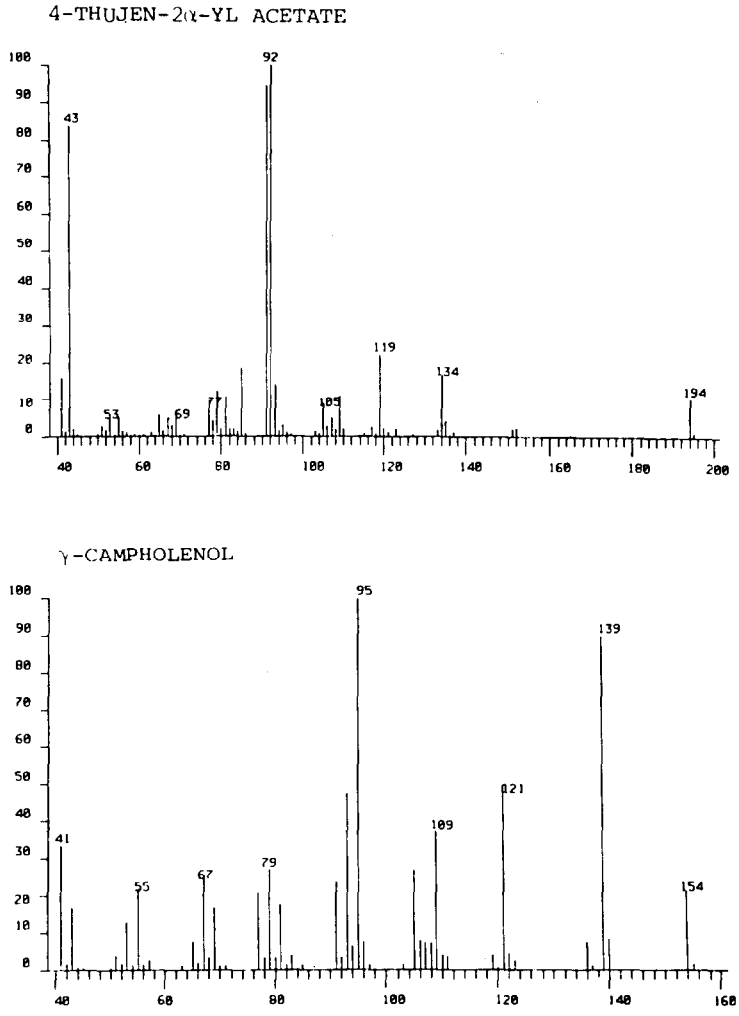

Fig. 1. Mass spectrum of 4-thujen-2α-yl acetate and γ-campholenol.

singlets (one belonging to the exocyclic double bond), three doublets (one CHOAc), three triplets (one belonging to the exocyclic double bond) and two quartets (methyl groups). The IR spectrum shows bands characteristic of a cyclopropyl ring (Fig. 2). Decoupling experiments in the presence of the shift reagent $Eu(fod)_3$ established the partial structure $CH_2{=}C(C){-}CH_2{-}CHOAc$ ($J_{H_2,H_3\alpha} = J_{H_2,H_3\beta} = 8$ Hz; $J_{H_3\alpha,H_3\beta} = 16$ Hz) in which the acetoxy group is likely to be in the α-position. On the basis of these data (see also [7, 8]), structure **2** is proposed for the acetate. Minor components in this oil were carvone and *trans*-carveol.

The main component of oil No. 448 ($[\alpha]_D^{20.5} +19.1°$) made up 95% of the oil. The ^1H NMR and IR spectra of this component were identical with those of (+)-davanone (**3**), a sesquiterpene ketone isolated from *Artemisia pallens* Wall. [9–13]. Unfortunately, the optical rotation of our sample of davanone has not been determined. Since (+)-davanone from *Artemisia pallens* Wall. has an $[\alpha]_D^{20}$ of about +81°, it is not certain that the two davanones have the same configuration. Essential oil No. 448 has bactericidal and fungicidal properties. At a concentration of 100 μg/ml, it is active against 18 strains of bacteria and one vibrio, while at a concentration of 50 μg/ml the growth of 16 strains of fungi are totally inhibited (all strains belonging to internationally standardized collections [2]).

Oil No. 469 ($[\alpha]_D^{20.5} -8.7°$) contained five major components which were identified as artemisia ketone (40%), artemisia alcohol (**4**, 25%), γ-campholenol (**5**, 10%), isopinocamphone (8%) [6], and yomogi alcohol (**6**) (8%) [14–16]. Although genotypes yielding oils consisting mainly of artemisia ketone, and those consisting mainly of a mixture of artemisia ketone and umbellulone have been found before [1], this is the first time that artemisia alcohol has been identified in *Tanacetum vulgare* genotypes.

The structure of artemisia alcohol was confirmed by reduction of artemisia ketone with sodium borohydride in methanol. The MS and also GC retention times of the product obtained were identical with those of the compound present in the essential oil. γ-Campholenol has been obtained synthetically by reduction of γ-campholenic aldehyde [17] or of γ-campholenic acid

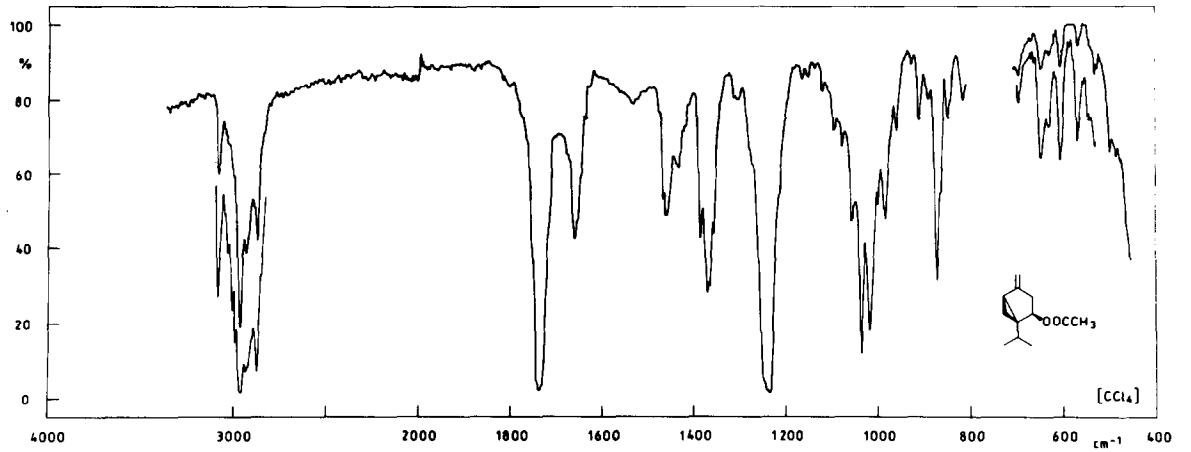

Fig. 2. IR spectrum of 4-thujen-2α-yl acetate.

[18]. However, to our knowledge, this product has not yet been isolated from plants. γ-Campholenic acid was reported as a constituent of olibanum oil [19].

EXPERIMENTAL

Plants were propagated by division, and the oils obtained as described previously [1]. Analytical GC was carried out with a JEOL JGC-810 gas chromatograph; glass columns (3 m × 5 mm i.d.), packed with 10% DEGS on Chromosorb W Sil 60–80 mesh, and with 10% OV-17 on Chromosorb G AW 60–80 mesh. Preparative GC was carried out with a Becker 409 instrument with FID and glass splitter; glass column (1.8 m × 5 mm i.d.), packed with 3% SE-30 on Gas-Chrom Q 80–100 mesh. Mass spectra (70 eV) were obtained with two instruments: (1) a JEOL JMS-D300/JGC-20K GC-MS system; the JGC-20K carrying glass columns (2 m × 5 mm i.d.), packed with 3% DEGS on Gas-Chrom W 100–120 mesh, and with 3% OV-1 on Chromosorb W HP 100–120 mesh; (2) a Kratos MS-80 GC/MS-DS-50 instrument; glass column (2 m × 5 mm i.d.), packed with 3% OV-1 on Gas-Chrom Q 80–100 mesh. Metastable ion spectra were recorded with a VG Micromass ZAB-2F instrument. NMR spectra (in $CDCl_3$ or CCl_4) were recorded with TMS as the internal standard; IR spectra in CCl_4. Optical rotations (as $[\alpha]_D^{20.5}$) were measured with undiluted oil in 10 mm cells.

Reduction of artemisia ketone. Artemisia ketone (20 mg) was stirred with $NaBH_4$ (10 mg) in MeOH (2 ml) for 2 hr at 0°. After addition of H_2O (5 ml) the soln was extracted with CH_2Cl_2 (×2). The organic layer was washed, dried and after removal of the solvent, pure artemisia alcohol was obtained.

Spectral data. MS of **2** and **5** are reproduced in Fig. 1, the IR spectrum of **2** is reproduced in Fig. 2.

^{13}C *NMR* (*in* $CDCl_3$). Artemisia alcohol (**4**): 145.0 (*d*, C-6), 136.0 (*s*, C-2), 124.1 (*d*, C-3), 113.0 (*t*, C-7), 74.5 (*d*, C-4), 41.8 (*s*, C-5), 25.9, 23.8, 21.2, 18.3 (*q*, four Me's).

γ-Campholenol (**5**): 136.5 (*s*, C-4), 136.2 (*d*, C-3), 62.7 (*t*, CH_2OH), 46.2 (*d*, C-1), 46.1 (*s*, C-2), 42.1 (*t*, C-5), 33.3 (*t*, CH_2CH_2OH), 28.1, 22.1 (*q*, geminal Me's), 16.7 (*q*, C-8).

trans-Carveyl acetate: 170.8 (*s*, CO), 148.7 (*s*, C-8), 130.9 (*s*, C-1), 127.8 (*d*, C-6), 109.2 (*t*, C-10), 70.7 (*d*, C-2), 35.8 (*d*, C-4), 33.7 (*t*, C-3), 30.9 (*t*, C-5), 21.4 (*q*, CH_3CO), 20.8, 20.6 (*q*, two Me's).

Lyratol (**1**) (lyratyl acetate): (170.8) (CO), 146.9 (146.5) (C-5), 139.4 (139.1) (C-8), 135.9 (131.2) (C-2), 125.8 (129.0) (C-3), 114.5 (114.8) ($CH=CH_2$), 110.6 (110.8) ($C=CH_2$), 68.7 (69.8) (C-1), 49.2 (49.2) (C-4), 21.0 (21.0), 13.9 (14.1) (two Me's), (21.0) (CH_3CO).

4-Thujen-2α-yl acetate (**2**): 171.0 (*s*, CO), 148.3 (*s*, C-4), 103.8 (*t*, C-10), 75.2 (*d*, C-2), 38.7 (*s*, C-1), 35.8 (*t*, C-3), 31.2 (*d*, C-7), 30.0 (*d*, C-5), 21.3 (*q*, CH_3CO), 20.0, 19.7 (*q*, two Me's), 14.7 (*t*, C-6).

Yomogi alcohol (**6**): 147.1 (C-6), 135.4, 134.5 (C-3 and C-4), 110.6 (C-7), 70.7 (C-2), 38.5 (C-5), 30.0, 27.1 (four Me's).

^1H *NMR* (*in* CCl_4). 4-Thujen-2α-yl acetate (**2**): δ 5.32 (*t*, $J = 8$ Hz; *d*, $J = 1.2$ Hz; 1 H, $CHOAc$), 4.58, 4.78 (2 H, $=CH_2$), 2.70 (*d*, $J = 16$ Hz; *d*, $J = 8$ Hz; 1 H, $CHCHOAc$), 1.98 (*s*, 3 H, CH_3CO), 0.92 and 0.90 (*d*, $J = 6.8$ Hz; 6 H, two $CHCH_3$'s).

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