COMPOUNDS OF THE PYRAN SERIES AS COMPONENTS OF THE ESSENTIAL OILS OF Tanacetum boreale AND Ajania fastigiata

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It has been established that the essential oils of Tanacetum boreale and Ajania fastigiata contain as their main components 3-hydroxy-2,2,6-trimethyl-6-vinyltetrahydropyran and its acylated and oxidized derivatives.

Three compounds have been isolated from the essential oils of Tanacetum boreals **Fisch** (arctic tansy) and Ajania fastigiata (Winkl) **Poljak** (Tanacetum fastigiata Poljak) growing in the Northern part of the Tien-Shan by fractional distillation and preparative gas chromatography.

An ester (I) ($\nu_{C=O}$ 1738 cm^{-1}, ν_{C-O} 1230 cm^{-1}), bp 98-99°C/10 mm Hg; n_D^{20} 1.4584, d_{20}^{20} 0.9945; $[\alpha]_D^{20}$ +17.5°.

Found, %: C 68.18; H 9.38; O 22.43; $C_{12}H_{20}O_3$.

Calculated, %: C 67.89; H 9.50; O 22.61.

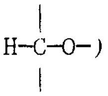
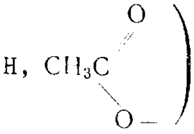
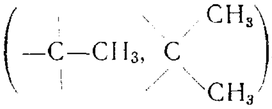
An alcohol (II) (ν_{OH} 3429 cm^{-1}), with bp 97-98°C/±0 mm Hg, n_D^{20} 1.4584; d_{20}^{20} 0.9896; $[\alpha]_D^{20}$+ 15.8°; composition $C_{10}H_{18}O_2$.

Mass spectrum: m/z (%), 170 (M$^+$, 0.04), 155 (M$^+$ − 15.4), 137 (3), 112 (5), 109 (7), 95 (10), 94 (60), 83 (11), 83 (10), 79 (14), 71 (10), 69 (15), 68 (100), 67 (35), 59 (68), 55 (20), 53 (13), 43 (47), 41 (23), 39 (12).

A ketone (III) ($\nu_{C=O}$ 1723 cm^{-1}) with n_D^{20} 1.4545; d_{20}^{20} 0.9649, $[\alpha]_D^{20}$ −9.3°; composition $C_{10}H_{16}O_2$; 2,4-DNPH, mp 111-112.5°C.

Mass spectrum: m/z (%), 168 (M$^+$, 0.1), 153 (M$^+$ − 15.3), 110 (44), 95 (7), 82 (19), 68 (100), 67 (68), 59 (9), 55 (11), 53 (10), 43 (23), 41 (16), 39 (10).

The IR spectra of the compounds isolated (Fig. 1) showed the absorption bands at 3090, 1830, 1640, and 920 cm^{-1} that are characteristic for a vinyl group. Bands at 1368 and 1380 cm^{-1} indicated the presence of geminal methyl groups [1]. The closeness of the IR spectra of the compounds permitted the assumption that they contained the same carbon skeleton. This was confirmed by chemical transformations. Saponification of the ester (I) with alcoholic alkali gave the alcohol (II), and oxidation of the latter with chromium trioxide yielded the ketone (III) [4].

The PMR spectrum of the ester: characteritic multiplet in the 4.7-6.1 ppm region (A_2B system, 1 H, 2 H, respectively, quaternary $-CH=CH_2$); triplet at 4.52 ppm (1 H, J ~ 3 Hz,  $H-\overset{|}{\underset{|}{C}}-O-$); singlet at 1.90 ppm, (3 H,  $CH_3C\overset{O}{\underset{O-}{\lessgtr}}$); multiplet with its center at 1.64 ppm (4 H, $-CH_2-CH_2-$); three singlets at 0.99, 1.06, and 1.11 ppm with intensities of 3 protons each belonging to quaternary methyl groups ( $-\overset{|}{\underset{|}{C}}-CH_3,\ \gtrless C\overset{CH_3}{\underset{CH_3}{<}}$). The downfield shift of the signals of the methyl groups is obviously due to a **neighboring ester oxygen**. In the PMR spectrum

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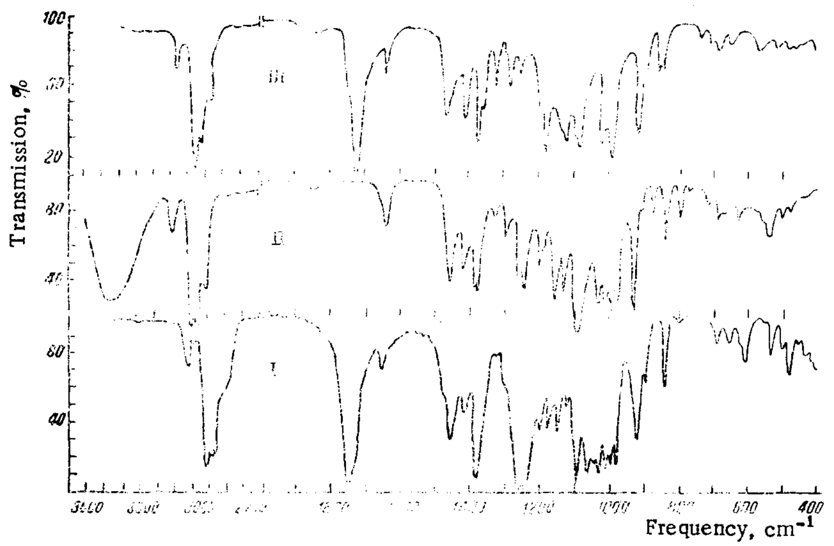


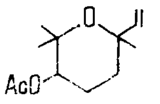
Fig. 1. IR spectra of 3-acetoxy-2,2,6-trimethyl-6-vinyltetrahydropyran (I), 3-hydroxy-2,2,6-trimethyl-6-vinyltetrahydropyran (II), and 3-oxo-2,2,6-trimethyl-6-vinyltetrahydropyran (UR spectrophotometer, thin layer – 0.008 mm).

of the alcohol (II) the signals of the methyl groups had fused into a nine-proton singlet at 1.15 ppm. This singlet split into two components in a ratio of 1:2 when the substance was dissolved in benzene.

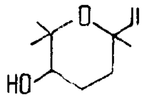
The signal of the hydroxy group was observed at 2.95 ppm, and the triplet of a proton geminal to it was shifted into the 3.20 ppm region. The magnitude of its spin–spin coupling, 4 Hz, indicated that this proton occupied the equatorial position in a ring [2] and, consequently, the hydroxy group was located in the axial position.

In the PMR spectrum of the ketone (III) the structure of a multiplet of the signals of a $-CH_2-CH_2-$ group in the 1.75 ppm region was clearly determined as that of A_2B_2 system.

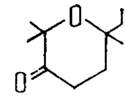
The results obtained on the compsoition and spectral characteristics of the substances isolated, and also the "isoprene rule" permitted the following most probable structure of tetrahydropyran derivatives to be proposed for the compounds described:



I



II



III

The positions of the functional groups in the molecules followed from the mass spectra of the alcohol and of the ketone. Thus, in the spectra of these compounds a m/z 68 ion was observed as the main one in each case. This was due to the formation of a stable methylbutadiene ion $CH_2=C(CH_3)-CH=CH_2$, which could not be obtained if the functional groups were present in position 3. Then an analysis of the mass spectra showed that m/z 155 = $M^+ - CH_3$; m/z 137 = $M^+ - H_2O - CH_3$; m/z 94 = $M^+ - H_2O - (CH_3)_2C=O$; m/z 110 = $M^+ - (CH_3)_2C=O$.

We obtained an independent proof of the structure of the compounds isolated by the addition to a solution of the alcohol in CCl_4 of a paramagnetic shift reagent, as which we used the dipivaloylmethane complex of europium. The nine-proton signals of the methyl groups then split into three three-proton components, with a faster downfield shift of two of them, belonging to gem-methyl groups.

By comparing the results obtained with information in the literature, we found that a similar composition and structure is possessed by a compound detected in the essential oil of the camphor tree Cinnamomum camphora [3]. However, the substance reported melts at 96-98°C. It is obvious that the essential oils of T. boreale and T. fastigiata contains a different – a liquid – stereoisomer and two of its derivatives.

In the essential oils under discussion, the 3-hydroxy-2,2,6-trimethyl-6-vinyltetrahydropyran was the main component and was present in both the free and in the bound states.

The ketone (III) was present in small amounts and could be separated from thujone and isothujone by preparative gas—liquid chromatography.

We are the first to have detected compounds of the pyran series in the essential oils of tansy.

EXPERIMENTAL

The mass spectra of the compounds was obtained on an MU-1202 instrument at an energy of the ionizing electrons of 70 eV, and the PMR spectra on a Tesla BS-487, 80 MHz, instrument (HMDS, solutions in CCl_4 and in benzene).

The isolation of the substances and the checking of their purity were performed on UKh-2, PAKhV-0,5, and Vyrukhrom chromatographs.

3-Acetoxy-2,2,6-trimethyl-6-vinyltetrahydropyran (I) was obtained in the pure state by the vacuum distillation of the essential oil of arctic tansy through a fractionating column (30 theoretical plates) and was also isolated from a fraction of the essential oil of Ajania fastigiata boiling at 93-100°C/10 mm by preparative GLC (200 × 0.7 cm; polyethyleneglycol-2000, 25%, INZ-600, 0.25-0.31 mm; 190°C).

3-Hydroxy-2,2,6-trimethyl-6-vinyltetrahydropyran (II) was isolated by preparative GLC under similar conditions from alcoholic fractions of the essential oil of T. boreale and A. fastigiata that were eluted with diether from alumina (activity grade II-III) and was also obtained by saponifying compound (I); 9.5 g of the ester was boiled with 150 ml of a 1 N ethanolic solution of caustic soda for 3 h. After the solution has been neutralized with dilute sulfuric acid, the compound was extracted with diethyl ether. The yield was quantitative.

3-Oxo-2,2,6-trimethyl-6-vinyltetrahydropyran (III) was isolated from the fractions of the essential oils boiling at 65-78°C/10 mm by preparative GLC (380 × 0.7 cm; PEG adipate, 25%; INZ-600, 0.25-0.31 mm; 180°C), and it was also obtained by the oxidation of the alcohol (II): at 20°C with stirring, 34 g of CrO_3 was added to a solution of 53.5 g of pyridine in 800 ml of methylene chloride and after 15 min 8.5 g of the alcohol in methylene chloride was added dropwise and stirring was continued for another 15 min. The resulting mixture was separated in a separatory funnel. The organic layer was washed with 5% NaOH solution (3 × 100 ml) and then successively with 100 ml portions of 5% HCl solution, 5% $NaHCO_3$ solution, and saturated NaCl solution, and was dried over $MgSO_4$.

SUMMARY

Tetrahydrofuran derivatives have been isolated for the first time from the essential oils of Tanacetum boreale and Ajania fastigiata.

LITERATURE CITED

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