| Terpene hydrocarbons | *G. platycarpum*, 1st fraction | % calculated on whole oil | *G. daucoides*, 1st fraction | % calculated on whole oil |
|---|---|---|---|---|
| α-Pinene | Tr. | Tr. | 2 2 | 1,5 |
| Camphene | Tr. | Tr. | — | — |
| Myrcene | Tr. | Tr. | Tr. | Tr. |
| β-Pinene | 15,6 | 1,0 | 7,2 | 5,0 |
| Sabinene | — | — | 2,8 | 2,1 |
| Limonene | 65,8 | 5,3 | — | — |
| o-Cymene | 5,2 | 0,3 | 52,2 | 32,7 |
| p-Cymene | 12,4 | 1,0 | 35,6 | 25,1 |

In the second fraction (with bp 61-65°C) of the essential oil of *G. platycarpum* linalool (80%) was identified, and in the high-boiling residue nerol, geraniol, linalyl acetate, and linalyl formate. The phenolic fraction of the essential oil of *G. daucoides* consisted mainly of carvacrol.

Thus, it has been established that the essential oil of *G. platycarpum* contains, in addition to substances detected previously, α- and β-pinenes, camphene, myrcene, o- and p-cymenes, nerol, and geraniol. This is the first time that the chemical composition of the essential oil of *G. daucoides* has been studied. It must be mentioned that the oils investigated of the two species of the genus *Grammosiadium* differ markedly in the composition of their chemical compounds, which is not characteristic for species of a single genus.

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# GERMACRANOLIDES OF *Tanacetum pseudoachillea*

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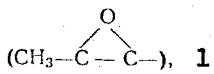
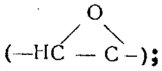
By chromatography on silica gel of the nonpolar fraction of an extract of the inflorescences of *Tanacetum pseudoachillea* C. Winkl. [1] with a mixture of hexane and ethyl acetate (9:1) we have isolated a substance with the composition $C_{20}H_{26}O_5$, mp 146-147°C (ethanol); $[\alpha]_D^{22}$ +42° (c 1.2; methanol), whichhas proved to be a new sesquiterpene lactone and has been named tanadin (I).

The IR spectrum of (I) shows absorption bands at ($cm^{-1}$) 1760 (γ-lactone carbonyl), 1710 and 1235 (α,β-unsaturated ester group), and 1672 and 1652 (double bonds). The mass spectrum has the peaks of ions with m/e: 346 ($M^+$), 263 $(M-83)^+$, 246 $(M-100)^+$, 231 $(M-100-15)^+$, 218 $(M-100-15-28)^+$, 213 $(M-100-15-28-15)^+$. The ion with m/e 246 is formed by the splitting out of an acyl radical, $C_5H_8O_2$, from the molecular ion. On further fragmentation, the acyl residue loses a $CH_3$ radical and a CO group. From the products of the alkaline hydrolysis of compound (I) we isolated an identified angelic acid, just as in the hydrolysis of tanacin and tanapsin [1].

The PMR spectrum of (I) (taken on a JNM-4H-100/100 MHz instrument in $C_5D_5N$, δ scale, ppm, 0 — HMDS) the following resonance signals were observed: 1.30, s, 3 H  $(\mathrm{CH_3{-}\overbrace{C{-}C}^{O}{-}})$, 1.79 and 1.86, s, 3 H each $(2CH_3{-}C{=}C{-})$; 1.96, d, 3 H, J = 7 Hz $(CH_3{-}CH{=}C{-})$; 2.76, q, 1 H, $J_1$ = 2.5, $J_2$ = 10 Hz  $(\mathrm{{-}H\overbrace{C{-}C}^{O}{-}})$; 3.36, m, 1 H (H-7); 4.41, m, 1 H (H08); 5.27, q, 1 H, $J_1$ = 3, $J_2$ = 10 Hz (H-3); 5.58, m 1 H (H-6); 5.80, d, 1 H, J = 3 Hz (H-13); 5.92, m, 1 H (H-18); 9.30, d, 1 H, J = 3 Hz (H-13').

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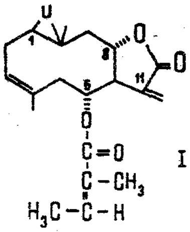
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 411-412, May-June, 1979. Original article submitted February 2, 1971.

Dihydrotanadin (II), $C_{20}H_{28}O_5$, mp 136-138°C, $M^+$ 348, was obtained by the reduction of compound (I) with sodium tetrahydroborate in methanol. IR spectrum of dihydrotanadin: $\nu_{max}^{KBr}$ 1770, 1710, 1238, 1652 $cm^{-1}$.

The germacrane skeleton of tanadin follows from its composition its PMR spectrum, and the production of chamazulene from dihydrotanadin.

A comparison of the PMR spectrum of tanadin with those of tanacin [2], acetylstizolin, and stizolicin [3] showed a similarity with these germacranolides. In contrast to the spectrum of tanacin, the PMR spectrum of tanadin has a quartet at 5.27 ppm — the signal of an olefinic proton — and a multiplet at 5.58 ppm due to a hemiacyl proton.

It follows from the facts given that tanadin differs from tanacin only by the position of the double bond and must have the structure (I).


I

On further elution of the column with hexane—ethyl acetate (4:1 and 2:1), we isolated a crystallizing mixture of two lactones (III) and tavulin [4]. Since it was impossible to separate this mixture by the usual methods, it was reduced with sodium tetrahydroborate in methanol. An individual liquid compound with the composition $C_{15}H_{22}O_3$, $M^+$ 250, was obtained. Acetylation of this with acetic anhydride in pyridine gave a substance with mp 141-143°C (from ethanol), $C_{17}H_{24}O_4$, $M^+$ 292, $[\alpha]_D^{22}$ +125.4° (c 1.1; methanol), which, according to its physicochemical constants, was identical with dihydrolaurenobiolide [5]. Thus, compound (III) is a mixture of deacetyllaurenobiolide and dihydrodeacetyllaurenobiolide [6, 7].

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