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SESQUITERPENE LACTONES OF *Inula caspica*

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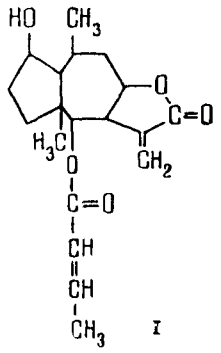
The flower heads and leaves of *Inula caspica* Blume. (Caspian inula) collected in the mass flowering phase in the Abral mountains, Semipalatinsk province, Kazakh SSR, were exhaustively extracted with chloroform. The resin isolated was treated with 60% ethanol. The resulting precipitate was separated off, and the lactones were extracted from the aqueous ethanolic solution with chloroform. The combined extractive substances obtained inhibited the growth of mustard seeds by 62% and completely suppressed the germination of wheatgrass seeds. The combined substances were chromatographed on a column of type KSK silica gel at a ratio of material to support of 1:15. When the column was eluted with benzene and with benzene–ether (1:1), two crystalline substances were isolated.

Substance (I) – $C_{19}H_{26}O_5$, mp 220-222°C (ethanol), $[\alpha]_D^{18}$ +116.9° (chloroform) was a new sesquiterpene lactone and we have called it incaspin. IR spectrum, ν_{max}^{KBr}, cm^{-1}: 3500 (–OH); 1750 (carbonyl of a γ-lactone); 1720, 1250 (ester group); 1670 (>C=C<). When (I) was dehydrogenated over 30% Pd–C at 330°C, chamazulene was obtained.

The PMR spectrum (taken on a Tesla BS-497 instrument in $CDCl_3$, 100 MHz, 0 – TMS) showed the following signals: singlet at 0.90 ppm (3 H) – angular methyl; doublet at 1.87 ppm (3 H) – secondary methyl group; doublet at 2.14 ppm (3 H) – methyl at a double bond of an ester group. A multiplet at 3.95 ppm (1 H) was assigned to H_6; a triplet of doublets at 4.57 ppm (1 H, J_1 = 2 Hz, J_2 = 5 Hz) to a lactone proton; a singlet at 4.70 ppm (1 H) to a hydroxylic proton; and doublets at 5.53 and 6.05 ppm (1 H each, $J_1 = J_2$ = 2 Hz) to the protons of an exocyclic vinyl group conjugated with the carbonyl of a γ-lactone. A singlet at 5.32 ppm (1 H) and a quartet at 5.58 ppm (1 H, J = 1.3 Hz) were characteristic for H_{17} and H_{18}, respectively.



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Substance (II) – $C_{19}H_{26}O_7$, mp 188-190°C (ethanol), $[\alpha]_D^{20}$ –26° (c 5.0; chloroform). From its IR, PMR, and ^{13}C NMR spectra and its physicochemical constants, substance (II) proved to be identical with the pseudoguaianolide britanin [4].

Only britainin has been isolated from this plant, by aqueous extraction [5].

In a concentration of $2 \cdot 10^{-6}$ M, britanin inhibited the germination of radish seeds by 87% of mustard by 85%, and of wild oats by 63%, and it completely suppressed the growth of

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the coleoptiles of wheat of the Saratovskaya 29 variety. At a concentration of 0.5%, britanin exhibited 100% repellance for the imago of the yellow mealworm beetle, and the degree of protection of a leaf was 85%.

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THE MAIN TRITERPENE COMPOUNDS OF VINE LEAVES AND RACHISES

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We have investigated the neutral triterpene components of hexane extracts of the leaves and rachises of the vine *Vitis vinifera* L. s., of the Rkatsiteli variety. The corresponding extracts, obtained with yields of 5 and 4%, respectively, were saponified by the usual method [1]. The unsaponifiable part contained 49.5% in the case of the extract from the leaves and 23.8% in the case of the extract from the rachises.

Chromatography on silica gel (the eluent being petroleum ether, containing increasing concentration of diethyl ether) yielded from both products a fraction of dimethyl- and methylsterols which were identified by using authentic compounds of these classes as markers in TLC. Since the fractions isolated proved to be complex mixtures of compounds (GLC), they were acetylated with acetic anhydride in pyridine and the acetates obtained were rechromatographed on silica gel impregnated with 5% of silver nitrate, using the same eluting system. Then the dimethylsterol fraction from the leaves yielded the acetates of taraxerol, of taraxasterol, and of β-amyrin, which were identified from their melting points and their PMR and mass spectra. These compounds were the main ones, and they were accompanied by small amounts of the acetates of β-amyrin, lupeol, and methyl oleanolate, which were identified from their mass spectra with the use of chromato-mass spectrometry (CMS) (for conditions, see [2]).

It was established by the CMS methed that the main components of the acetylated fraction of the methylsterols from the leaves were the acetates of citrostadienol and of 24-ethyllophenol.

Similarly, from the mixture of acetates of the dimethylsterols from the vines rachises we isolated the acetates of α- and β-amyrins and of lupeol, and by the CMS method we identified the acetates of taraxerol, tarazasterol, germanicol, cycloartenol, and 24-methylenecycloartanol. By the CMS method, the fraction of methylsterols from the rachises were found to contain citrostadienol, obtusifoliol, and oleanic and ursolic aldehydes.

This is the first time that any of the compounds identified apart from the last two [3] have been identified in *Vitis vinifera* L.s.

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