GUAIANOLIDES OF *Lactuca tatarica*

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In the pharmacopeias of some European countries the milky juice of plants of the genus *Lactuca* has long been known as a sedative under the name of "lettuce opium," its active principle being a sesquiterpene lactone of the guaiane type, lactucin [1, 2].

Representatives of the genus *Lactuca* growing on the territory of the USSR have not hitherto been studied. In the present paper we give the results of an investigation of the epigeal organs of Tartarian lettuce (*Lactuca tatarica* L.) – one of the species most widely distributed in Central Asia [3].

To isolate the lactones, the epigeal part of this plant (10 kg) gathered in the period of mass flowering in the valley of the R. Amu Darya (Chardzhou province, Turkmen SSR) in August, 1985, was exhaustively extracted with ethanol. The total yield of extractive substances from the air-dry mass of the plant was 816 g (8.16%). The concentrated extract was purified with 60% aqueous alcohol. The precipitate that had deposited was separated off, and the compounds to be investigated were extracted from the filtrate with chloroform. The total neutral substances so obtained (127 g) were chromatographed on a column of KSK silica gel (100-200 mesh) at a ratio of substances to support of 1:10. The fractions (500 ml each) from chromatographic separation were distributed in the following sequence: 1-10 (hexane); 11-14 [hexane–ethyl acetate (9:1)]; 15-28 [hexane–ethyl acetate (4:1)]; 29-56 [hexane–ethyl acetate (7:3)]; 57-73 [hexane–ethyl acetate (3:2)]; 74-90 [hexane–ethyl acetate (1:1)]; 91-109 (ethyl acetate); 110-135 [ethyl acetate–ethanol (1:1)].

Fractions 11-14 contained substance (I) with the composition $C_{30}H_{50}O$, mp 186-187°C (from alcohol). Mass spectrum: m/z 426 (M^+), 411, 408, 356, 314, 272, 257, 218, 207, 203, 199. The peaks of ions with m/z 218, 207, and 203 indicated that the compound belonged to the pentacyclic triterpenoids of the α,β-amyrin series. On the basis of chemical and spectral characteristics the compound isolated was identified as α-amyrin [4, 5].

From fractions 56-63 crystals of a lactone (II) deposited with the composition $C_{23}H_{22}O_7$. mp 132°C (from ethanol, with decomposition).

The IR spectrum of (II) (KBr tablets) exhibited absorption bands at 3420, 3165, 1770, 1740, 1680, 1625, 1600, 1520, 1270, and 1240 cm^{-1}.

Mass spectrum: m/z 410 (79%, M^+), 258 [47, M^+ – p-hydroxyphenylacetic acid (152)], 240 (13, $M^+ - 152 - 18$), 229 (9, $M^+ - 152 - 29$), 212 (9, $M^+ - 152 - 18 - 28$), 152 (100), 107 (35). (The ejection of p-hydroxyphenylacetic acid was confirmed by a metastable peak with m/z 107).

The PMR spectrum of (II) ($Py\text{-}d_5$) showed the signals of a secondary methyl group at a double bond, and of lactone, gem-hydroxylic, conjugated olefinic, and aromatic protons, and also of an exocyclic methylene of a γ-lactone ring.

From its physicochemical properties and spectral characteristics, substance (II) was identified as the guaianolide lactucopicrin [6].

Fractions 66-73 contained lactone (III) with the composition $C_{15}H_{16}O_5$, mp 212-213°C (from alcohol). IR spectrum: 3370, 3270, 1770, 1670, 1615 cm^{-1}.

In the mass spectrum of (III) there were characteristic peaks with m/z 276 (M^+), 258 ($M^+ - 18$), 240 ($M^+ - 18 - 18$), 229, and 212, showing that lactone (III) was deacylated lactone (II), which has been described in the literature under the name of lactucin [2, 7]. The PMR spectral characteristics of lactone (III) were also identical with those of lactucin [7]. The amounts of the lactones isolated, calculated on the air-dry raw material were (%): (II) – 0.1; (III) – 0.02. Thus, the plant *Lactuca tatarica* L. gathered in the Turkmen SSR contains

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lactones analogous to those isolated from other lettuce species growing in the countries of Central Europe [1, 2].

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3,7,8,15-TETRAHYDROXY-12,13-EPOXYTRICHOTHEC-9-EN IN A CULTURE OF Fusarium graminearum

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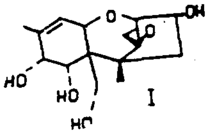
In an investigation of the metabolites formed by an isolate of Fusarium graminearum Schw. (479a VNIIZ [All-Union Scientific-Research Institute of Grain and the Products of its Processing]) on grain, together with the previously known 3,7,15-trihydroxy-12,13-epoxytrichothec-9-en-8-one (4-deoxynivalenol) and its 3-acetyl and 15-acetyl derivatives [1], we have found a new substance, 3,7,8,15-tetrahydroxy-12,13-epoxytrichothec-9-en (I).



I

The production of the biomass, extraction, and absorption purification of the extract were carried out as described previously [1]. The extract, purified in this way that had been obtained from 0.7 kg of dry biomass was then subjected to LC on a column of silica gel L (3.5 × 100 cm; 100-400 μm; 250 g) in a gradient mobile phase (1 liter each of mixtures of benzene and acetone in the form of successive 10% additions, with the collection of 200-ml fractions). The eluate obtained from the use of benzene–acetone (60:40) was evaporated to a dry residue, which was dissolved in 200 ml of chloroform and extracted with water (3 × 200 ml). The aqueous extract was evaporated to an oily residue (4.71 g). This residue was subjected to LC on a column of silica gel L (1.5 × 25 cm; 40-100 μm; 15 g) in the isocratic regime with the mobile phase chloroform–methanol (9:1), 10-ml fractions being collected.

The compositions of the fractions were monitored by TLC on Silufol in the mobile phases chloroform–methanol (7:1) (A) and benzene–acetone (2:3) (B). The substances were detected by means of a qualitative reaction for an epoxide group after the treatment of the Silufol plates with a 3% solution of 4-nitrobenzylpyridine (150°C, 30 min) and a 10% solution of tetraethylenepentamine in chloroform–carbon tetrachloride (2:3) [2].

The eluate fractions from the column that contained as their main component a substance with R_f 0.24 (A) were combined and evaporated to a dry residue (1.2 g), and then LC was conducted on a column of silica gel L (1.5 × 25 cm; 40-100 μm; 15 g) in a gradient mobile phase (100 ml each of mixtures of benzene and acetone in the form of 5% additions). The eluates from the column at a benzene:acetone ratio of 70:30, which contained a substance with R_f 0.22

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