

## URSOLIC ACID IN CERTAIN PLANTS

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In the investigation of certain plants growing in the Leningrad region (see below) we have detected a triterpene widely distributed in the plant world, ursolic acid with the composition  $C_{30}H_{48}O_9$ , which we identified by its melting point, the results of elemental analysis, IR spectra, and a mixed melting point with an authentic sample. The ursolic acid from *Empetrum nigrum* L. and *Thymus serpyllum* L. has been described previously [1, 2].

We isolated ursolic acid by the usual method [2]. The chloroform extract was evaporated to small bulk and treated with 5% caustic potash. The alkaline extract was acidified and the acids liberated were extracted with ether. The solvent was evaporated and the dry residue was crystallized from ethyl alcohol.

plant	Part of the plant
<i>Campanula rotundifolia</i> L.	} Epigeal
<i>Knautia arvensis</i> (L.) Coult.	
<i>Sambucus racemosa</i> L.	} Roots
<i>Siringa vulgaris</i> L.	
<i>Lonicera tatarica</i> L.	
<i>Epilobium angustifolium</i> L.	Epigeal
<i>Cassandra calyculata</i> Don.	Leaves
<i>Antennaria dioica</i> (L.) Gaertn.	} Epigeal
<i>Empetrum nigrum</i> L.	
<i>Thymus serpyllum</i> L.	

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## THE GLYCOSIDES OF ELEUTHEROCOCCUS SENTICOSUS

### II. The Structure of Eleutherosides A, B<sub>1</sub>, C, and D

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In a preceding communication [1], a method was described for obtaining from the roots of *Eleutherococcus senticosus* Max a physiologically active glycosidic fraction from which a number of glycosides provisionally called "eleutherosides" were isolated in the individual state.

As previously shown [2], eleutheroside E is identical with acanthoside D, which is a diglucoside of (-)-syringaresinol [3].

Eleutheroside A, mp 295°C,  $[\alpha]_D^{20}$  -35° (in pyridine) has been identified as daucosterol from its melting point and analytical, spectroscopic, and chromatographic data. Daucosterol has previously been isolated from ginseng [4] and acanthopanax [5].

Eleutheroside B<sub>1</sub>, mp 218°C,  $[\alpha]_D^{20}$  +80° (in methanol), can easily be obtained from fractions enriched in a mixture of eleutherosides B and B<sub>1</sub> by fractional crystallization or by chromatography on silica gel previously impregnated with aqueous ammonia (pH 9.0) using gradient elution with the solvent system chloroform saturated with aqueous ammonia (pH 8.5-9.0), ethanol (100: 0 → 50: 50). The acid hydrolysis of eleutheroside B<sub>1</sub> yielded glucose and a genin  $C_{11}H_{10}O_5$ .

The genin of eleutheroside B<sub>1</sub> was identified as isofraxidin (7-hydroxy-6,8-dimethoxycoumarin), which has been isolated from the roots of *Fraxinus excelsior* [6] and was then obtained by the hydrolysis of calycanthoside (isofraxidin

7- $\beta$ -glucoside), mp 219–220°C,  $[\alpha]_D^{20} -42^\circ$  (in methanol), a glycoside from the branches of Calycanthus occidentalis [7]. Eleutheroside B<sub>1</sub> differs from calycanthoside only by its specific rotation and is therefore its anomer.

Eleutheroside C, mp 140°C,  $[\alpha]_D^{20} +186^\circ$  (in water), has been identified as methyl  $\alpha$ -D-galactoside by means of its analytical data, specific rotation, chromatographic behavior ( $R_f$  value and coloration of the spots), and its IR spectrum. Ethyl  $\alpha$ -D-galactoside has previously been isolated from the seeds of lupins and has been called galactite [8].

Eleutherosides D and E, differing slightly in their  $R_f$  values, are completely identical with respect to melting point, analytical data, and IR and UV spectra. Thin-layer chromatography of the genins formed by the hydrolysis of eleutherosides D and E have shown that they are identical. It is likely that eleutheroside D consists of a more soluble crystalline form of eleutheroside E; it is not excluded that the two compounds differ only in configuration.

Thus, a methanolic extract of the roots of Eleutherococcus senticosus contains representatives of very different classes of natural compounds and this evidently explains the breadth of the pharmacological action of an extract of Eleutherococcus root.

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#### AN INVESTIGATION OF THE ALKALOIDS OF UNGERNIA TRISPHERA, NARCISSUS TAZETTA, N. KRISTALLI, and N. FOLLI

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In a study of the alkaloids of the genus Ungernia (family Amaryllidaceae), we have investigated the leaves of U. trisphaera collected in the early vegetation period in the Kaakha Region of the Turkmen SSR, and three species of Narcissus, also belonging to this family.

From the leaves of U. trisphaera, in addition to the licorine and hippeastrine obtained previously [1], we have isolated tazettine, pancratine, hordenine [2, 4], and two substances of nonalkaloid nature. One of them has been identified as acetamide [2], and the second (mp 67–68°C), an optically inactive substance with the composition  $C_{31}H_{64}$ , proved to be n-hentriacontane [3]. This is the first detection of the latter in plants of the family Amaryllidaceae. These substances were separated by making use of their different solubilities in organic solvent.

Then we investigated the plant N. tazetta, gathered in the basin of the River Shargun in the Surkhandar Oblast by the botanist S. Khamidkhodzhaev. Licorine and pancratine were isolated from the leaves and bulbs of N. tazetta in addition to the tazettine [5] previously found by Späth [5].

After the dying off of the epigeal part, the bulbs of N. kristalli taken from the Botanical Gardens of AS UzSSR contained 0.27% of total alkaloids. Chromatography on a column of alumina [with elution by means of benzene and a mixture of benzene and ethyl acetate (1:1)] gave five alkaloids (table). The bulbs of N. folli were found to contain 0.45% of alkaloids (33% of the total consisted of licorine). Of course, the leaves that had died off of the species of Narcissus that we investigated contained no alkaloids.