URSOLIC AND 3-EPIURSOLIC ACIDS FROM WASTES FROM THE PRODUCTION OF LAVENDER OIL

B. N. Kal'yan and G. V. Lazur'evskii

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, pp. 53–54, 1968

As reported previously [1] we have isolated from lavender (population N 13 of the Nikita Botanical Garden) a mixture of ursolic and 3-epiursolic acids. Recently, the 3-epi isomer has been obtained by German workers [2] semisynthetically from ursolic acid.

We have now developed a method for the separation of the mixture isolated into its epimers. The raw material for the work was the calyxes of lavender taken after the essential oil had been distilled from the plant. They were dried in the air and extracted with petroleum ether and then with ethanol. The ethanolic extract (yield 3.1% of the weight of the calyxes) formed a green amorphous powder consisting mainly of impure ursolic and 3-epiursolic acids. The mixture of acids was freed from impurities by passing an ethereal solution of the extract through a column of Norite (100 g of extract to 400 g of Norite). This gave 68 g of a white powder which, after four recrystallizations from methanol–toluene (3:2) was chromatographed on silica gel. For this purpose, 10 g of the substance was dissolved in benzene and transferred to a column containing 500 g of adsorbent. Benzene–ether (9:1, and then 8:2) eluted 3-epiursolic acid (1.09 g). After three recrystallizations from methanol, the substance had mp 238–239° C, $[\alpha]_D^{20}$ + 65° (in chloroform). These figures agree with those given in the literature [2]. Ether eluted the ursolic acid.

The two hydroxy acids were identified by means of their IR spectra [3] and their derivatives, methyl esters, acetates, and acetates of the methyl esters. To confirm the difference in the configurations of the molecules at the third asymmetric center, the ursolic and 3-epiursolic acids were interconverted. For this purpose, each of the acids was oxidized with chromic anhydride in pyridine. In both cases, ursonic acid was obtained. The reduction of this with sodium borohydride gave ursolic acid. However, when the ursonic acid was reduced by the Meerwein-Ponndorf method with subsequent chromatographic separation of the reduction products on silica gel, 3-epiursolic acid was obtained. This confirms literature data according to which the hydroxy group in 3-epiursolic acid occupies the axial position and that in ursolic acid the equatorial position.

3-Epiursolic acid has not previously been found in nature; we have described the first case of its isolation from a plant.

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18 July 1967

Kishinev Polytechnic Institute

UDC 615.43+615.177/779

THE CONTENT OF ARBUTIN IN SOME SPECIES OF THE GENUS SERRATULA

Ya. K. Yatsyuk, S. S. Lyashenko, and V. S. Batyuk

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, p. 54, 1968

From the leaves of Serratula isophylla Claus (family Compositae) by chromatography on Kapron we have isolated a phenolic glycoside $C_{12}H_{16}O_7$ with mp 146–147° C, $[\alpha]_D^{20}$ −60° C. Its acetyl derivative $C_{22}H_{26}O_{12}$ contains five acetyl groups and has mp 146° C, $[\alpha]_D^{20}$ −28.2° (in acetone).

The dry residue of an ethyl acetate extract of a concentrated aqueous extract of the raw material that had previously been purified with chloroform was subjected to chromatography. The column was washed with chloroform until the eluate was colorless, after which elution was carried out with a mixture of chloroform–ethanol–acetic acid (900:100:1). The combined eluates were evaporated and the dry residue was recrystallized several times from water. The glycoside crystallized in the form of thin white needles.

When the glycoside was hydrolyzed with 2% sulfuric acid for 4 hr, an aglycone $C_6H_6O_2$ with mp 170–171° C was obtained. The acetyl derivative $C_{10}H_{10}O_4$ contained two acetyl groups and had mp 121° C.

From its Rf value and its color reactions on paper chromatography in various solvent systems, the aglycone was identical with a reference sample of hydroquinone. Mixtures of the aglycone with hydroquinone and of its acetate with hydroquinone acetate gave no depression of the melting point.

Enzymatic hydrolysis with an enzyme from the fungus Aspergillus oryzae again gave hydroquinone and D-glucose, in equimolecular amounts.

Like arbutin, the glycoside that we had isolated gave a blue coloration with ferric chloride. The Rf values and the nature of the coloration of the glycoside on paper chromatography in various solvent systems coincided with those of a reference sample of arbutin. Mixtures of the glycoside with arbutin isolated from the leaves of Arcostaphylos uva ursi and of their pentaacetates gave no depression of the melting points.

We have also found arbutin in the leaves of S. bracteifolia Stank. and S. xeranthemoides MB.

8 June 1967

Zaporozh'e Pharmaceutical Institute

UDC 547.918

SEPARATION OF THE GLYCOSIDES OF GINSENG ON BIO-GEL P-2

G. B. Elyakov, N. I. Uvarova, V. P. Krysina, and L. M. Antonik

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, pp. 54–55, 1968

To separate the total glycoside fraction (TGF) from the roots of ginseng (Panax ginseng C. A. Meyer) [1], we have used gel filtration through Bio-Gel P-2 (50–100 mesh) [2].

Distribution of the glycosides in the fractions		Glycosides contained in the fractions (panoxosides)
fraction	g	
1—20	—	—
21—22	0.1158	*D*, *E*, *F* and *G*
23—32	0.1486	*F* and *G*
33—34	0.0078	Traces of *F* and *C*
35—50	0.5076	*A*, *B* and *C*
51—63	0.0723	Traces of *A*, *C* and *F*

The Bio-Gel (200 g), after being swollen in a 0.1 N solution of sodium chloride (24 hr) was transferred to a column (75 × 3.5 cm) and washed with distilled water. One gram of TGF in methanol (5 ml) was transferred to the column and

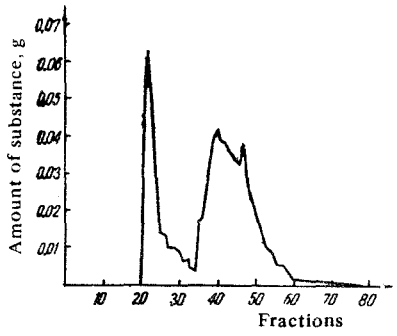

Fig. 1. Distribution of TGF of ginseng on Bio-Gel P-2.

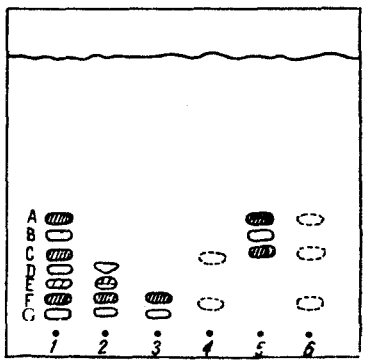

Fig. 2. Thin-layer chromatogram of the combined fraction obtained in the distribution of the TGF of the roots of ginseng on Bio-Gel P-2. 1) TGF; 2) fractions 21-22; 3) fractions 23-32; 4) fractions 33-34; 5) fractions 35-60; 6) fractions 61-63. Solvent system: chloroform–methanol (2:1) saturated with water. Spots visualized with concentrated H_2SO_4.