

COMPONENTS OF *Libanotis buchtormensis* (FISCH.) D.C. FRUITS*

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From the light petroleum extract of *Libanotis buchtormensis* (FISCH.) D.C. fruits paraffins, terpenic hydrocarbons, coumarins (bergapten, imperatorin, isoimperatorin, bergaptol, osthol, isoaculeatin, mexotycin, xanthotoxin), sesquiterpenic alcohols (nerolidol, bisabolol, eudesmol) and β -sitosterol were isolated.

In connection with a more detailed investigation of the *Libanotis* genus (*Umbelliferae*) and taxonomically closely related species we investigated the light petroleum extract of the fruits of *L. buchtormensis* (FISCH.) D.C. This species is a perennial plant growing in mountainous areas of west and east Siberia, Central Asia and Mongolia. Little data is available in literature on the components of the fruits and they concern only the general occurrence of coumarins¹ and the essential oil². Further data on the components of this plant concern mainly coumarins in the roots (*cf.*³⁻⁶).

The light petroleum extract was separated by column chromatography on deactivated silica gel. The least polar fraction, representing about 18% of the weight, was a mixture of paraffins and terpenic hydrocarbons. Both groups of substances were separated chromatographically on silica gel impregnated with silver nitrate and analysed by GLC with reference samples. The presence of n-alkanes from C₂₀ to C₃₁ was detected in the mixture of saturated hydrocarbons, with the C₂₇ and C₂₉ components predominating. The mixture of unsaturated hydrocarbons consisted of limonene, *p*-cymene and caryophyllene. Further chromatographic fraction containing ester compounds according to IR spectroscopy consisted mainly of fats. GLC analyses of the methyl esters of fatty acids indicated the presence of predominantly C_{16:0}, in addition to C_{18:2}, C_{18:1}, and C_{18:0}. According to the IR spectra⁷ the subsequent more polar fractions contained furocoumarins – bergaptene and xanthotoxin. Further fractions, characterized by the presence of a considerable amount of hydroxyl groups afforded nerolidol and bisabolol on chromatography.

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The last but one fractions eluted from the starting chromatography of the crude extract contained according to the IR spectra both alcohols and furocoumarins, in accordance with the isolation of eudesmol, and isoimperatorin. Finally, the furocoumarins osthol, imperatorin, bergaptol, and isoaculeatin were isolated from the most polar chromatographic fractions and identified by IR and mass spectra. In addition β -sitosterol was also isolated.

EXPERIMENTAL

Kofler block for the m.p. determination (uncorrected) and Zeiss UR-20 (Jena) infrared spectrophotometer, AEI MS 902 mass spectrometer, Varian XL-200 (200 MHz) ^1H NMR spectrometer, and Packard 427, Perkin-Elmer F 11 and Pye 104 gas chromatographs were used for spectral and analytical measurements. Silica gel for column chromatography was of 40–60 μ , deactivated by addition of 11% of water. The herbarium specimen of *L. buchtormensis* is deposited in the Botanical Institute of the Mongolian Academy of Sciences, Ulan Batar.

Chromatography of the light petroleum extract: Dry not completely ripe fruits of *L. buchtormensis* (580 g), collected at the beginning of August 1983 in the mountains of Mongolian Altai (Bajan-Olgij ajmak), were extracted exhaustively with light petroleum (40–60°C). Evaporation of the solvent gave 18 g of the extract. A part (15 g) was chromatographed on silica gel (800 g). Eluent: Light petroleum with a gradient of ether. 26 fractions were collected.

Hydrocarbons: The combined fractions 1–4 (2.7 g) were rechromatographed on silica gel impregnated with silver nitrate. The saturated hydrocarbons, eluted with light petroleum, were analysed by means of GLC using a glass column 185 \times 0.24 cm packed with Gas Chrom Q (100–200) and impregnated with 3% OV-101 as stationary phase. The programmed temperature was from 150–280°C/2°C/min. Identification was carried out by comparison with a standard mixture of n-paraffins. A mixture of unsaturated hydrocarbons was eluted with light petroleum–ether (4 : 3) and analysed by means of GLC, using a capillary column 50 m \times 0.5 mm with an OV-17 phase, programmed temperature 130–210°C/2°C/min. Identification was carried out by comparison with a standard mixture.

Fats: Fraction 5–8 (1.6 g) showed in its IR spectrum the presence of a band at 1752 cm^{-1} . A part of the fraction (100 mg) was converted to methyl esters and analysed by GLC using a glass column 0.24 \times 185 cm packed with a Gas-Chrom 80–100 support, wetted with 5% Silar-10 C. The programmed temperature was 80–210°C, with a temperature increase of 4°C/min. When compared with a standard mixture the presence of predominantly $\text{C}_{16:10}$ was detected in addition to $\text{C}_{18:2}$, $\text{C}_{18:1}$, and $\text{C}_{18:0}$.

Bergaptene, xanthotoxin: Fractions 10–13 (2 g) had a characteristic fluorescence in the UV light. Its IR spectrum displayed bands at 1727, 1628, 1590 cm^{-1} . Column chromatography on silica gel afforded in the first fractions a substance with m.p. 186°C (methanol). Mass spectrum: m/z 216. Its IR spectrum was identical with the spectrum of authentic bergaptene⁷. From further fractions a compound was isolated with m.p. 147–148°C and the mass spectrum m/z 216. According to its IR spectrum it was identified as xanthotoxin⁷.

Nerolidol, bisabolol: Fraction 14–17 (4 g) contained a strong peak of the OH group in its IR spectrum (3530, 3608 cm^{-1}). Rechromatography on a hundredfold amount of silica gel and subsequent preparative separation on TLC plates (silica gel impregnated with silver nitrate) gave two alcohols which were identified on the basis of IR spectra, mass spectra and elution times in GLC as nerolidol and bisabolol.

Eudesmol, isoimperatorin: Fraction 18–21 (1.8 g) displayed an OH peak in its IR spectrum (3 610, 3 222 cm^{-1}) and the presence of coumarins (1 582, 1 627, 1 610 cm^{-1}). Rechromatography on silica gel (ethyl acetate–light petroleum) gave eudesmol. Identification was carried out by means of IR spectrum⁸, as well as by comparison of its R_F value in GLC with a standard. The more polar substance, eluted with ethyl acetate–light petroleum (7 : 93) and melting at 109°C (from methanol), was identified on the basis of its mass, IR and ¹H NMR spectra as isoimperatorin.

Osthol, imperatorin, β -sitosterol, bergaptol, isoaculeatin: Combined fraction 22–26 (2.1 g) contained according to IR spectrum (1 582, 1 610, 1 627 cm^{-1}) predominantly coumarins. Rechromatography on silica gel (elution with chloroform) gave gradually the following compounds: m.p. 80–83°C (methanol), according to mass spectrum identified as osthol; m.p. 101–104°C (methanol), according to mass spectrum identified as imperatorin; m.p. 139°C (acetone), according to mass and IR spectrum identified as bergaptol; m.p. 153–156°C (methanol), according to mass spectrum identical with isoaculeatin; m.p. 194°C (methanol), identified as mexotacin⁶.

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