UDC 547.99/581.19

FUROCOUMARINS OF THE FRUIT OF HIPPOMARATHRUM CASPIUM

G. V. Pigulevskii, Yu. A. Dranitsyna, S. Sh. Kerimov, and I. S. Kozhina

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 4, p. 277, 1967

The present paper gives the results of a study of the furocoumarin compounds [1] from the fruit of this plant which we collected on the seashore dunes close to Sumgait (AzerbSSR) at the end of August 1964.

The chloroform extraction (by the steeping method) [2] of 580 g of fruit gave 133.7 g of resin (23.0% of the air-dry weight of the material). The resin was chromatographed on a column of alumina (1:11). The substances were eluted from the column successively with petroleum ether (fractions 1–17), petroleum ether–chloroform, 4:1 (fractions 18–74), chloroform (fractions 75–84), and ethanol (fractions 85–97). The volume of each fraction was 200 ml.

Fractions 1–5 yielded a mixture of essential and fatty oils. Fractions 6–29 contained isoimperatorin, yield 0.62%. Fractions 30–67 gave imperatorin with a yield of 0.17%, bergapten, and xanthotoxin. Fractions 68–74 consisted of a mixture of three substances which was rechromatographed on a column of alumina (1:100) with petroleum ether–chloroform (7:3) as eluant. Bergapten (total yield 0.40%), xanthotoxin (total yield 1.45%), and isopimpinellin with a yield of 0.13% were isolated.

These substances were shown to be identical with known furocoumarins by their IR and UV spectra, their elemental composition, their R_f values on paper chromatography with reference samples, and by the absence of depressions of the melting points of mixtures with corresponding samples of furocoumarins that we isolated from the fruit of the Hippomarathrum microcarpum [2]. In addition, the identity of the imperatorin was confirmed by the production from it of alloimperatorin [3] and xanthotoxol [4].

It was established by paper chromatography that fractions 75–97 contained traces of umbelliferone.

REFERENCES

1. S. Sh. Kerimov and Yu. A. Dranitsyna, KhPS [Chemistry of Natural Compounds], 356, 1965.
2. Yu. A. Dranitsyna, S. Sh. Kerimov, and G. V. Pigulevskii, ZhPKh, 38, 1172, 1965.
3. E. Späth and H. Holzen, Ber., 66, 1137, 1933.
4. Yu. A. Dranitsyna, ZhPKh, 33, 984, 1960.

3 December 1966

Komarov Botanical Institute;
Lenin Dagestan University

UDC 547.99/58.19

COUMARINS OF THE SEEDS OF CORONILLA SCORPIOIDES

Yu. N. Beletskii and N. F. Komissarenko

Khimiya Prirodnykh Soedinenni, Vol. 3, No. 4, pp. 277–278, 1967

The isolation from the seeds of Coronilla scorpioides (L) Koch. (scorpion coronilla) of the cardenolides corotoxigenin, frugoside, glucocorotoxigenin, a glycoside (IV), and coronillobioside, which are steroid compounds of the trans-A/B series, has been reported previously [1].

The present paper gives the results of a study of the coumarin compounds of this species of Coronilla.

Six substances of coumarinic nature were detected by paper chromatography of alcoholic extracts of the seeds in the chloroform–formamide system: A (R_f 0.95), B (R_f 0.82), C (R_f 0.71), D (R_f 0.61), E (R_f 0.28), and F (R_f 0.15).

The coumarins were isolated by the method given. The seeds were extracted with 70% alcohol and the organic layer was evaporated off under vacuum. Substance B deposited from the aqueous residue. Treatment of the aqueous

extract with petroleum ether gave A, and on extraction with chloroform the other substances (C, D, E, and F) passed into the organic phase and were separated on silica gel (stationary phase – formamide; mobile phase – chloroform) to give substances C, D, and E.

Substance A (psoralen), $C_{11}H_6O_3$, mp 164–165° C, fluoresced on the paper chromatogram in UV light. Before treatment with alkali it was pale blue, and after treatment golden yellow.

On the basis of its R_f values in various solvent systems, IR spectra, and mixed melting points, substance A proved to be identical with psoralen (furo [6, 7: 2', 3'] coumarin).

Substance B (daphnoretin), $C_{19}H_{12}O_7$, mp 254–256° C, fluoresced on a paper chromatogram in UV light. Before treatment with alkali it was pale blue and after treatment the fluorescence disappeared almost completely. The substance formed a monoacetyl derivative ($C_{21}H_{14}O_8$, mp 240–242° C) and a methyl derivative ($C_{20}H_{14}O_7$, mp 239–241° C). On decomposition in a current of hydrogen [2], it was converted into umbelliferone and scopoletin.

From its physicochemical properties and conversion products, the substance under investigation was identified as daphnoretin (6-methoxy-7-hydroxy-3, 7'-dicoumaryl ether) [2].

Substance D (scopoletin), $C_{10}H_8O_4$, mp 200–202° C, fluoresced on the paper chromatogram in UV light pale blue both before and after spraying with alkali. From its physicochemical properties and R_f values this substance was identified as scopoletin (6-methoxy-7-hydroxycoumarin) [3].

Substance E (umbelliferone), $C_9H_6O_3$, mp 223–224° C. The methylation of this compound gave a substance with composition $C_{10}H_8O_3$ and mp 117–118° C, identical with herniarin (7-methoxycoumarin).

From the physicochemical properties of the starting material and its derivatives, it was identified as umbelliferone (7-hydroxycoumarin) [4].

REFERENCES

1. Yu. N. Beletskii, Farm. zhurnal USSR, no. 1, 22, 1964.
2. R. Tschesche, U. Schacht, and G. Leger, Ann., 113, 662, 1963.
3. R. Seka and P. Kallir, Ber., 64, 909, 1931.
4. N. F. Komissarenko and D. G. Kolesnikov, Ninth Mendeleev Congress. Abstracts of Papers and Communications [in Russian], no. 4, 271, 1965.

1 March 1967

Kharkov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.972

FLAVONOIDS OF LARIX DAHURICA. I

N. A. Tyukavkina, K. I. Lapteva, and V. A. Pentegova

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 4, pp. 278–279, 1967

The heartwood of Larix dahurica (Dahurian larch) ground to dust (28.5 kg with a moisture content of 24.94%), taken from two trees 128 and 156 years old in the Chita Oblast was exhaustively extracted with acetone. The dry extract (1.16 kg) was treated successively with absolute acetone, ether, and benzene. The substances insoluble in ether (699.09 g or 3.2% of the dry wood) and in benzene (150.65 g or 0.75%) were taken for study. From the results of ascending paper chromatography [Leningrad slow paper, formic acid–acetic acid–water (10: 2: 3) system] and thin-layer chromatography on Kapron [methanol–CCl_4 (15: 85) system], these two fractions were similar in the number and qualitative composition of the flavonoid components.

Individual substances were isolated by preparative chromatography on Kapron powder. The ratio of adsorbent to total substances chromatographed was 30: 1, and the process was monitored by thin-layer chromatography. The concentration of methanol was increased from 15 to 50 vol. %. The flavonoids, recrystallized from aqueous ethanol, were identified by their melting points, elemental compositions, and chromatographic behaviour in the presence of reference samples (the authors are grateful to E. Rudloff (Canada) for kindly providing samples of dihydroquercetin and dihydrokaempferol). The samples obtained were dried at 110° C and a residual pressure of 10^{-3}–10^{-4} mm Hg for 20–22 hr.