

NATURAL MERANZIN HYDRATE - A NEW COMPONENT
OF THE ROOTS OF *Prangos ferulacea*

A. Z. Abyshev, P. P. Denisenko,
N. P. Kostyuchenko, A. I. Ermakov,
and Yu. N. Sheinker

UDC 577.15/17;582.89

In an investigation of a methanolic extract from the roots of *Prangos ferulacea* (L.) Lindl, we have isolated four individual compounds (I-IV) giving a positive reaction for coumarin derivatives. The present paper gives the results of a study of the structure of (I).

Substance (I), $C_{17}H_{20}O_6$, mp 135-137°C (from benzene), $[\alpha]_D^{20} + 81.12$ (c 1.26; chloroform), possesses a bright blue fluorescence in UV light and apparently belongs to the coumarin group.

The IR spectrum of (I) has absorption bands at (cm^{-1}) 3545 (OH); 1725 (C=O of an α -pyrone ring); 1605, 1565, 1495 ($-C=C$ bond in an aromatic ring); 1405, 1380, 1365 (gem-dimethyl group). In the nature of the distribution of the absorption bands in the 1500-1625 cm^{-1} region, the IR spectrum of (I) is very similar to the spectra of osthole, meranzin, meranzin hydrate, and pranferin [1, 2], which shows that this substance is a 7,8-disubstituted coumarin.

The presence of a hydroxy group in the molecule of (I) is confirmed by the formation of an acetyl derivative (V), $C_{19}H_{22}O_7$, mp 83.5-85°C (from benzene-petroleum ether).

The NMR spectrum of (I) (Fig. 1) has the following signals: singlets at δ 1.25 ppm (6 H), 1.67 ppm (3H), and 3.93 ppm (3H) corresponding to a $O-C(CH_3)_2$ gem-dimethyl grouping and to $-OCOCH_3$ and $-OCH_3$ groups, respectively; and a multiplet at δ 3.10 ppm (2H) and a quartet at δ 5.10 ppm (1H) due to the methylene and methine protons in a $-CH_2-CH-O$ grouping. In the region of aromatic signals there are doublets corresponding to the protons at C_3 and C_4 (δ_3 6.16; δ_4 7.82 ppm, $J_{3,4}=10$ Hz) and at C_5 and C_6 (δ_5 7.47; δ_6 6.96 ppm; $J_{5,6}=9$ Hz) (1H each). The signal of a hydroxy group is found in the form of a broadened singlet at δ 3.71 ppm (1H).

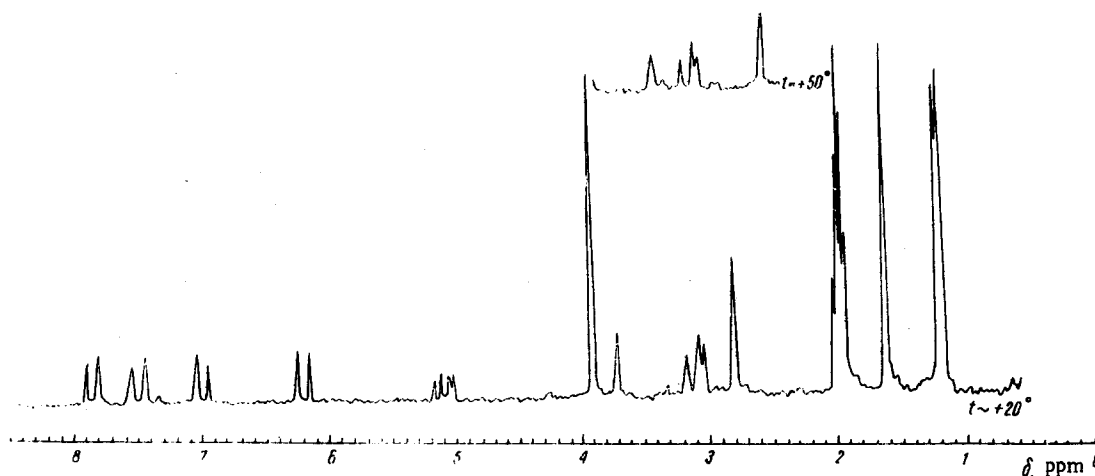
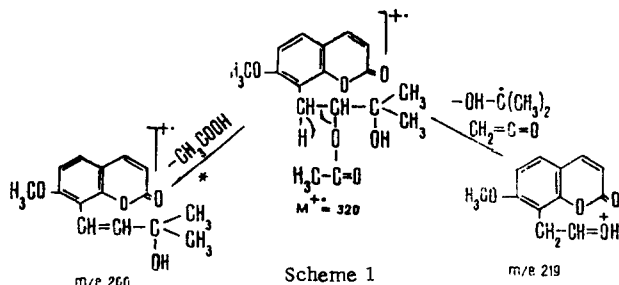


Fig. 1. NMR spectrum of (I).

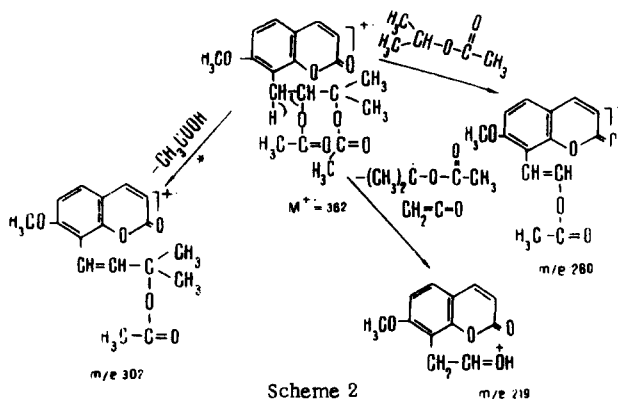
Leningrad Sanitary-Hygienic Medical Institute. S. Ordzhonikidze All-Union Chemical and Pharmaceutical Scientific-Research Institute. Translated from *Khimiya Prirodnikh Soedinenii*, No. 5, pp. 608-612, September-October, 1972. Original article submitted January 31, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

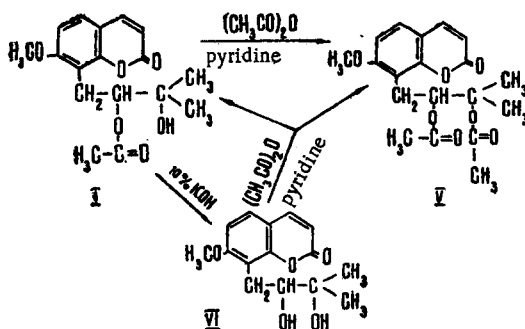
In a mass-spectrometric study, we found that (I) undergoes the decomposition characteristic for acetylated coumarins [3].



The value of M^+ found is 320 m/e. The presence of a peak with m/e 43 ($\text{CH}_3-\text{C}\equiv\text{O}^+$) in the mass spectrum of (I) (Fig. 2a) shows that this compound is in fact an acetate. A comparison of the mass spectrum of (I) with the spectrum of ulopterol acetate [3], and also the IR and NMR spectra, permit the conclusion that (I) is an isomer of the latter; i.e., it is 8-(2'-acetoxy-3'-hydroxyisopentyl)-7-methoxycoumarin.



A peculiar feature of the fragmentation of (I) and its acetate (V) (see Fig. 2b) is shown in the elimination from M^+ of a molecule of acetic acid with the formation of ions having m/e 260 ($m^* = 211$) and m/e 302 ($m^* = 252$), respectively (schemes 1 and 2).



The structure found corresponds to meranzin hydrate monoacetate [4]. This is confirmed by the absence of a depression of the melting point of a mixture with an authentic sample and by the similarity of their IR spectra. When (I) was saponified with 10% KOH in methanol, meranzin hydrate (VI), $\text{C}_{15}\text{H}_{18}\text{O}_5$, mp 126°C (from benzene), which we have previously isolated from the roots of the plant under investigation [4], was formed.

The acetylation of (VI) under the usual conditions, as reported previously [4], forms a monoacetyl derivative; however, when a sample of (VI) was subjected to prolonged heating (8-10 h) with acetic anhydride in pyridine, a diacetate was also obtained, with mp $83.5-85^\circ\text{C}$, which was shown to be identical with (V) by a mixed melting point and by their IR spectra. The study of the other three substances (II-IV) is continuing.

EXPERIMENTAL

The IR spectra were taken on Perkin-Elmer 457 and UR-20 spectrometers (paraffin oil), the NMR spectrum on a JNM-4H-100 spectrometer (deuteroacetone, HMSO as internal standard), and the mass spec-

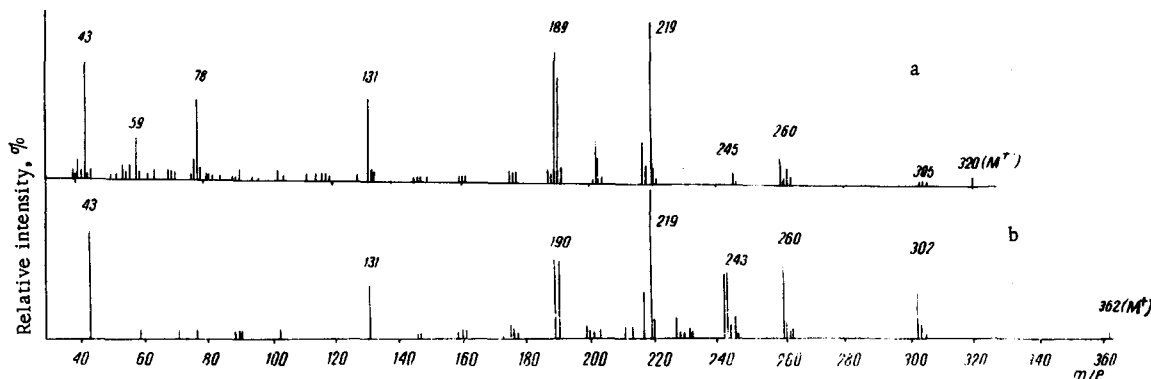


Fig. 2. Mass spectra of (I) (a) and (V) (b).

trum on an MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source at an ionizing voltage of 30 eV. The melting points were determined on a Kofler block. The elementary analyses of all the compounds corresponded to the calculated figures.

Isolation of the Coumarins. The comminuted roots of *Prangos ferulacea* (L.) (0.5 kg) were extracted with methanol (2 × 1 liter). The methanol was distilled off under vacuum, and the resulting residue (27 g of resin) was chromatographed on a column of alumina (200 g; activity grade V). Elution was performed with benzene (fractions 1-8), benzene-chloroform (1:1) (fractions 9-14), chloroform (fractions 15-21), and methanol (fractions 22-26). The volume of each fraction was 50 ml. The compositions of the fractions were determined by thin-layer chromatography [Al_2O_3 , activity grade III, ethyl acetate-benzene (1:2 and 1:1) and ethyl acetate systems].

Isolation of (I). After the solvent had been distilled off, fractions 15-21 yielded crystals of (I). After recrystallization from benzene, mp 135-137°C, $[\alpha]_D^{20} + 81.12^\circ$ (c 1.26; chloroform), R_f 0.32 [Al_2O_3 , activity grade III, ethyl acetate-benzene (1:1)]. The mother solution, by preparative separation in a thin layer of alumina, yielded (II) with mp 119-121°C (from petroleum ether), R_f 0.84 [Al_2O_3 , activity grade II, ethyl acetate-benzene (1:4)], possessing a yellow fluorescence in UV light.

Isolation of (III) and (IV). After the distillation of the solvent, the methanolic fractions yielded a mixture of (III) and (IV), which was re-separated on a column of alumina (activity grade V). In this way, substances (III) and (IV) were isolated in the individual state. In UV light they have a bright-blue fluorescence and they are apparently liquids, since attempts to crystallize them from various solvents proved unsuccessful. $R_{f\text{III}}$ 0.27; $R_{f\text{IV}}$ 0.65 (Al_2O_3 , activity grade III, ethyl acetate).

Acetylation of (I). A mixture of 0.5 g of (I), acetic anhydride (5 ml), and pyridine (2 ml) was heated for 2 h. After working up by the usual method, the reaction mixture was chromatographed on a microcolumn of alumina. This gave (V) with mp 83.5-85°C [benzene-petroleum ether (1:1)], R_f 0.51 [Al_2O_3 , activity grade III, ethyl acetate-benzene (1:4)].

Alkaline Hydrolysis of (I). A mixture of 0.1 g of (I) and 10 ml of 10% KOH in methanol was heated for 30 min, then the methanol was evaporated off, and the residue was dissolved in water. After acidification with conc. HCl, the reaction product was extracted with ether. The ether was washed with water and dried over sodium sulfate. The solvent was distilled off under vacuum. This gave (VI) with mp 126°C (from benzene), identical with meranzin hydrate.

Acetylation of (VI). A mixture consisting of 0.03 g of (VI), 2 ml of acetic anhydride, and 0.5 ml of pyridine was heated for 2 h. By the usual method, the reaction products yielded, after recrystallization from benzene, a substance with mp 135-137°C, identical with (I). After prolonged heating (8-10 h), a substance with mp 83.5-85°C was also isolated from the reaction mixture, and it was shown to be identical with (V) by a mixed melting point and by the similarity of their IR spectra.

SUMMARY

Four compounds (I-IV) of coumarin nature have been isolated from a methanolic extract of the roots of *Prangos ferulacea* (L.) Lindl.

A study of IR, NMR, and mass spectra, and also chemical properties, has shown that (I) is 8-(2'-acetoxy-3'-hydroxyisopentyl)-7-methoxycoumarin, identical with the monoacetyl derivative of meranzin hydrate; this is the first time it has been found in nature. The investigation of the structure of compounds (II-IV) is continuing.

LITERATURE CITED

1. A. Z. Abyshv, P. P. Denisenko, N. Kostyuchenko, O. S. Anisimova, A. I. Ermakov, and Yu. N. Sheinker, *Khim. Prirodn. Soedin.*, 675 (1970).
2. G. A. Kuznetsova and A. Z. Abyshv, *Khim. Prirodn. Soedin.*, 283 (1965).
3. A. Z. Abyshv, A. M. Kutnevich, N. P. Kostyuchenko, O. S. Anisimova, A. I. Ermakov, and Yu. N. Sheinker, *Khim. Prirodn. Soedin.*, 300 (1970).
4. G. A. Kuznetsova and A. Z. Abyshv, *Zh. Prikl. Khim.*, 38, No. 10, 2370 (1965).