The study of the lignan glycosides of pine needles is continuing.

LITERATURE CITED

1. S. A. Medvedeva, S. Z. Ivanova, V. G. Gorokhova, S. K. Votintseva, V. A. Babkin, and N. A. Tyukavkina, Khim. Drev., 3, 91 (1983).
2. M. Chiba, S. Hisada, S. Nishibe, and H. Thieme, Phytochemistry, 19, 335 (1980).
3. K. Miki, T. Takehara, T. Sasaya, and A. Sakakibara, Phytochemistry, 19, 449 (1980).

COUMARINS FROM THE HERBAGE OF TURKMENIAN SPECIES OF THE GENUS *Achillea*

V. V. Shmatova, A. I. Derkach,
M. O. Karryev, and N. F. Komissarenko

UDC 577.15/17:582.89

In an investigation of the herbage of two species of the genus *Achillea* (*A. biebershteinia* Afan. and *A. krasheninnikovii*) from the family *Asteraceae* collected in the flowering period in the environs of Nokhur village, Bakharden region, Turkmen SSR, substances of a benzo-α-pyrone nature have been isolated. A series of substances fluorescing blue and green-blue in UV light was detected by paper chromatography.

To isolate these substances, the herbage of *Achillea biebershteini* was extracted with a tenfold amount of 95% ethanol and the ethanolic extract was evaporated until the solvent had been eliminated completely, after which the residue was treated with distilled water (1:2) and the aqueous solution was extracted successively with chloroform, diethyl ether, and ethyl acetate.

The chloroform extract (fraction 1) was evaporated and the residue was tranferred to a column of polyamide (1:30). Elution was performed with benzene and the with benzene—chloro-fomrm and benzene—ethanol.

The extraction and separation of the substance from *Achillea krasheninnikovii* were performed similarly.

As a result three substances were isolated from the chloroform fraction of these plants.

Substance (I) = $C_9H_3O_6$, mp 228-230°C. From its physicochemical properties it was identified as umbelliferone (7-hydroxycoumarin) In UV light it fluoresced bright blue [1].

Substance (II) - $C_{10}H_8O_4$, mp 204-205°C. On the basis of its physicochemical properties and those of its acetyl derivatives and their UV spectra, this compound was identified as scopoletin [2].

Substance (III) had the empirical formula $C_{10}H_8O_4$. In view of the identical elementary composition and close R_f values in a number of solvent systems of the substance isolated and scopoletin, it was assumed that this substance was an isomer of scopoletin — 6-hydroxy-7-methoxycoumarin.

The subsequent methylation of esculin with dimethyl sulfate showed that substance (III) was identical with 6-hydroxy-7-methoxycoumarin [3].

Thus, from the epigeal parts of *A. biebersteinii* and *A. krasheninnikovii* we have isolated the hydroxycoumarine, umbelliferone, scopoletin, and isoscopoletin for the first time. The structures of the substances isolated were confirmed by the results of UV and IR spectroscopy and acid and alkaline hydrolyses, and also by comparison with authentic samples.

LITERATURE CITED

1. M. O. Karryev and N. F. Komissarenko, Izv. Akad. Nauk TSSR, Ser. Biol. Nauk, No. 1, 65 (1981).

Institute of Botany, Academy of Sciences of the Turkman SSR, Ashkhabad. All-Union Scientific-Research Institute of Drug Chemistry and Technology, Khar'kov. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 561, July-August, 1985. Original article submitted January 29, 1985.

0009-3130/85/2104 0526$09.50

2. N. F. Komissarenko, Khim. Prir. Soedin., 142 (1969).
3. É. Ya. Martynenko, N. V. Lobko, and N. F. Komissarenko, Vinodelie i Vinogradarstvo SSSR, 2, 51 (1982).

3,4-METHYLENEDIOXY-5-METHOXYPROPIOPHENONE AND TERPENOID COUMARINS OF Ferula caucasica

S. V. Serkerov, F. A. Rasulov,
M. G. Pimenov and M. G. Belyi

UDC 633.82/88

We have investigated the roots of Ferula caucasia Korov. (Caucasian giant fennel) collected on the multicolored outcrops in the basin of the R. Chikil-chai (Azerbaidzhan SSR). The species F. caucasia, which is close to F. caspica Bieb., has not previously been studied chemically.

Three substances (I-III) were isolated from the resin of the roots by chromatography on a column of neutral alumina (4 × 110 cm, activity grade IV) with elution by hexane, hexane–chloroform (9:1) and (1:3), and chloroform. When fractions 42-44 (eluted by hexane–chloroform 1:3) were rechromatographed on a column of alumina (3.5 × 50 cm) with elution by hexane–chloroform (1:1), chloroform, and chloroform–ethyl acetate (9:1), another two substances (IV and V) were isolated in the individual state. The volume of the fractions collected was 100 ml.

Substance (I) – $C_{11}H_{12}O_4$, mp 91-92°C (from hexane) – was isolated from fractions 9-13 eluted by hexane–chloroform (9:1). Its IR spectrum showed absorption bands at (cm^{-1}) 1685 (CO of a ketone group conjugated with an aromatic ring); 1630, 1605, 1518 (C=C of a benzene ring); 2800 (methylenedioxy group), and 2860 (methoxy group).

The NMR spectrum contained the signals of a CH_3–CH_2–group (t, 1.10 ppm, 3 H, and q, 2.76 ppm, 2 H, J = 7 Hz), of a methylenedioxy groups (s, 5.91 ppm, 2 H), of a methoxy group (s, 3.83 ppm, 3 H), and of an aromatic ring (d, 6.94, and d, 7.07 ppm, 1 H each, J = 2 Hz).

Substance (II) – $C_{24}H_{32}O_5$, mp 212-214°C (from ethanol) – was isolated from fractions 49-53 eluted by hexane–chloroform (1:3). Its IR spectrum had the absorption bands of OH groups (3430 cm^{-1}), of the CO of an α-pyrone (1710 cm^{-1}), and of the C=C bonds of an aromatic ring (1620, 1560, 1520 cm^{-1}).

Substance (III) – $C_{24}H_{32}O_5$, mp 221-222°C (from ethanol) – was isolated from fractions 54-58 eluted by chloroform. In the region of characteristic frequencies of the IR spectrum were observed the bands of OH groups (3440, 3370 cm^{-1}), of the CO of an α-pyrone (1700 cm^{-1}), and of an aromatic ring (1620, 1560, 1510 cm^{-1}).

Substance (IV) – $C_{24}H_{28}O_4$, mp 184-185°C (from chloroform) – was eluted by chloroform when fractions 42-44 were rechromatographed. In the region of characteristic frequencies the IR spectrum of compound (IV) had the absorption band of a CO of an α-pyrone (1730 cm-1) and those of an aromatic ring (1620, 1520 cm^{-1}). OH groups were absent.

Substance (V) – $C_{29}H_{38}O_6$, mp 176-178°C (from ethanol) – was isolated from the fractions eluted by chloroform–ethyl acetate (9:1). The IR spectrum revealed the bands of OH groups (3350, 3500 cm^{-1}), of the CO group of a δ-lactone (1720 cm^{-1}), and of an aromatic ring (1625, 1513 cm^{-1}).

A direct comparison of the IR and NMR spectra, and also of the physicochemical constants, of substance (I-V) with those of 5-methoxy-3,4-methylenedioxypropiophenone (latifolone, crocatone) [1-4], ferucrin [5], isosamarkandin [6], badrakemone [7], and isosamarkandin angelate [8], respectively, showed the identity of the compounds compared.

Benzo-α-pyrone derivatives and farnesiferol A have been isolated previously from Caspian giant fennel, which is morphologically close to Caucasian giant fennel [9, 10].

V. L. Komorarov Institute of Botary, Academy of Sciences of the Azerbaidzhan SSR, Baku. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 561-562, July-August, 1985. Original article submitted March 6, 1985.

0009-3130/85/2104-0527$09.50