10. C. V. Holland, D. Horton, M. J. Miller, and N. S. Bhacca, J. Org. Chem., 32, 3077 (1967).
11. H. Paulsen and F. Leupold, Carbohydr. Res., 3, 47 (1966).
12. L. D. Hall, Chem. Ind. (London), 950 (1963).
13. R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLauchlan, J. Chem. Soc., 3699 (1962).
14. R. U. Lemieux, Can. J. Chem., 39, 116 (1961).

GALLOMYRICITRIN – A NEW ACYLATED FLAVONOID FROM *Sedum selskianum*

G. G. Zapesochnaya and G. P. Shnyakina

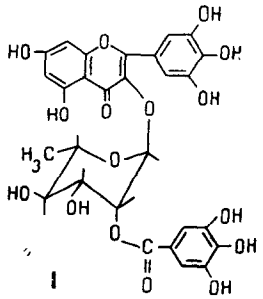
UDC 547.972

We have previously reported the isolation from the epigeal part of Sedum selskianum Rgl. et Mask. of the flavonoids myricitrin [1] and brassidin, and a new compound, which we called gallomyricitrin [2].

Gallomyricitrin (I) has the composition $C_{28}H_{24}O_{16} \cdot 2H_2O$, mp 214-216°C, $[\alpha]_D^{20} -40°$ (c 0.6; methanol). The acid hydrolysis of (I) gave the aglycone myricetin, L-rhamnose, and gallic acid. UV spectroscopy showed that the myricetin has one substituent in position 3. The acetylation of (I) gave a decaacetate (II) with the composition $C_{48}H_{44}O_{26}$, mp 136-138°C.

The NMR spectrum of (II) (Fig. 1) showed the signals of H-2',6' of myricetin and of H-2''',6''' of gallic acid (two-proton singlets at 7.78 and 7.68 ppm), and two doublets with J = 2.5 Hz of H-6 (6.8 ppm) and H-8 (7.3 ppm) of myricetin. In the 0.95-ppm region there is a doublet (J = 6 Hz) of the CH_3 group of rhamnose; the other protons of rhamnose resonate in the 3.3-5.9 ppm region: H-1'' and H-2'' as a multiplet with its center at 5.92 ppm, H-3'' as a quartet at 5.26 ppm ($J_{2,3}$ = 3 Hz, $J_{3,4}$ = 10 Hz), H-4'' as a triplet at 4.92 ppm ($J_{3,4} = J_{4,5}$ = 10 Hz), and H-5'' as a quartet at 3.32 ppm ($J_{5,6}$ = 6 Hz, $J_{4,5}$ = 10 Hz). Among the signals of the ten acetoxy groups two signals stand out at δ 1.95 and 1.98 ppm which are due to the carbohydrate part of the molecule and a singlet of the 5-OAc flavonoid part of the molecule (2.4 ppm); the other seven, aromatic, acetyl groups resonate in the 2.26-2.32 ppm region.

The results of a comparison of the chemical shifts and of the coupling constants of the carbohydrate protons of the TMS other (I) and the acetate (II) (see Fig. 1) with the values obtained for the acetates and TMS ethers of the 3-O-α-L-rhamnopyranosides of myricetin and quercetin permit the conclusion that in compounds (I) the L-rhamnose has a pyranose ring and the 1C conformation. A small coupling constant of the anomeric proton is possible for both the α and the β anomers; however, the magnitude and sign of the angle of optical rotation excludes the β form. The presence of only two singlets of aliphatic AcO groups in the spectrum of (II) and also of the signal of the hemiacyl proton (triplet at 5.6 ppm) in the TMS ether of (I) show that the gallic acid is attached to the rhamnose, and the spin–spin coupling constant in the triplet ($J_{1,2}$ = 2 Hz, $J_{2,3}$ = 2.5 Hz) enables it to be assigned to H-2'' of rhamnose. Thus, the gallic acid acylates the hydroxyl in position 2 of the rhamnose. On the basis of the facts presented, the following structure can be proposed for gallomyricitrin:



I

All-Union Scientific-Research Institute of Medicinal Plants. Khabarov State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 720-722, November-December, 1975. Original article submitted August 30, 1974.

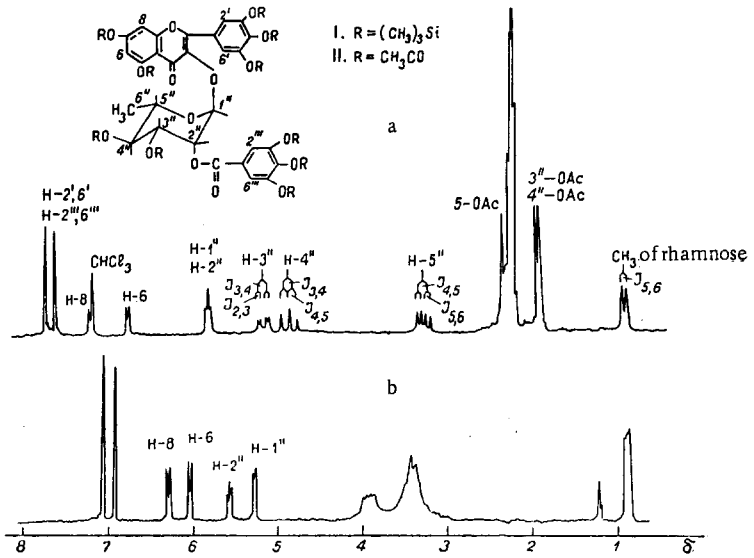


Fig. 1. NMR spectra of gallomyricitrin: a) TMS ether in CCl_4; b) decaacetate in $CDCl_3$ (internal standard – HMDS).

EXPERIMENTAL

The following instruments were used for recording the spectra: Varian HA-100D (NMR), Varian CH-8 (mass), Hitachi EPS-3T (UV), and UR-20 (IR). The purity of the substances was checked by chromatography on paper, silica gel, and polyamide. The results of elementary analysis agreed with the calculated figures.

Isolation. The epigeal part of Sedum selskianum collected in the flowering phase in the Maritime Territory was extracted with ethanol, and the extract was evaporated, diluted with water, and reextracted successively with ether and ethyl acetate. The aqueous phase was evaporated to small volume and deposited on polyamide, after which 30% ethanol eluted brassidin [2]. The residue from the ethyl acetate extract was chromatographed on polyamide. The column was washed with chloroform, and then a mixture of methanol and chloroform (1 : 9) eluted myricitrin (III) [1]. On further elution (15-30% methanol), a mixture of (I) and (III) was eluted, and this was separated by chromatography on polyamide in aqueous ethanol systems. The eluates obtained with 30-40% ethanol yielded yellow crystals of gallomyricitrin (I) with the composition $C_{28}H_{24}O_{16} \cdot 2H_2O$ mp 214-216°C, $[\alpha]_D^{20} - 40°$ (c 0.6; MeOH). ν_{CO} 1660, 1710 cm^{-1}. UV spectra (cm^{-1}): MeOH 355, 295 inflection, 267; NaOAc 381, 274; NaOAc + H_3BO_3 377; $AlCl_3$ 394; $AlCl_3$/HCl 358.

The trimethylsilyl (TMS) ether of (I) was obtained by a standard method [3]. The NMR spectrum of the TMS ether of (I) is given in Fig. 1.

Acid Hydrolysis of (I). Compound (I) (20 mg) was hydrolyzed with 5% HCl at 90°C for 1 h, and then the precipitate of the aglycone was filtered off and recrystallized from ethanol. This gave myricetin, $C_{15}H_{10}O_8$, mp 342°C (decomp.), identified by mass spectrometry: M^+ 318, the lateral phenyl fragment m/e 153. The hydrolyzate was found to contain L-rhamnose (PC and TLC with markers) and gallic acid: blue coloration with $FeCl_3$; the ions M^+ 170 and $(M - CO_2)^+$ 126 in the mass spectrum.

Acetylation and Preparation of the Decaacetate (II). A mixture of 20 mg of (I), 0.3 ml of pyridine, and 0.8 ml of acetic anhydride was kept at 20°C for 24 h and poured onto ice, the precipitate was washed with water and dissolved in acetone, and the solution was passed through a column containing 0.3 g of Al_2O_3 and the eluate was evaporated and recrystallized from ethanol. This gave the decaacetate (II), $C_{48}H_{44}O_{26}$, mp 136-138°C. ν_{CO} 1660, 1745, 1790 cm^{-1}. The NMR spectrum is given in Fig. 1.

SUMMARY

The new acylated flavonoid gallomyricitrin (I) with the composition $C_{28}H_{24}O_{16} \cdot 2H_2O$, mp 214-216°C, $[\alpha]_D^{20}$ – 40° (ethanol) has been isolated for the first time from Sedum selskianum. The structure of 2',3,3',4',5,7-hexahydroxyflavone 3-O-(2''-O-galloyl)-α-L-rhamnopyranoside is proposed for (I).

LITERATURE CITED

1. G. P. Shnyakina and G. G. Zapesochnaya, Khim. Prirodn. Soedin., 673 (1973).
2. G. P. Shnyakina and G. G. Zapesochnaya, Khim. Prirodn. Soedin., 92 (1975).
3. T. J. Mabry et al., The Systematic Identification of Flavonoids, Springer, New York (1970).

THE STRUCTURE OF VULGAROL – A NEW DITERPENOID FROM *Marrubium vulgare*

D. P. Popa and G. S. Pasechnik

UDC 547.913

We have previously [1] reported the isolation from the plant mentioned in the title (family Labiatae) of a new minor diterpene glycol $C_{20}H_{36}O_2$, which was called vulgarol. In the present paper we give results which enable us to establish structure (I) for this compound.

According to IR and mass spectrometry, vulgarol contains one trisubstituted double bond and two hydroxy groups.

On reaction with acetic hydride in pyridine, it readily forms a monoacetate, $C_{22}H_{38}O_3$ (II), and oxidation with active manganese dioxide converts it into an aldehyde (III), which shows the presence in the molecule of one primary allyl alcohol group.

The great similarity of its IR and mass spectra to the spectra of labd-13-ene-8α, 15-diol (IV), and also the presence in its NMR spectrum of the signals of five methyl groups characteristic for the labdane skeleton, give grounds for considering that vulgarol must have the labdane carbon skeleton (without taking stereochemistry into account).

The hydrogenation of vulgarol on platinum in ethyl acetate led, as also in the case of the diol (IV) [2], to two dihydro derivatives (V) and (VI) and a hydrogenolysis product (VII). The latter has similar IR spectra and identical R_f values to 13(RS)-tetrahydroabienol (VIII). However, these substances differ by their specific rotations, and a mixture of them gave a depression of the melting point.

Thionyl chloride dehydration of the monoacetate (II) yielded a diene (IX) with an exocyclic double bond; the IR spectra of this compound and of the acetate (X) are identical in the 800-1800 cm^{-1} region and differ only in the region of C–H vibrations (2800-3000, 700-800 cm^{-1}). However, the specific rotations of these substances are opposite in sign (Table 1).

The hydroxylation of vulgarol with osmium tetraoxide gave a tetrol (XI), which was converted by oxidation with periodic acid and potassium permanganate into a lactone (XII) differing from norambreinolide both in its constants and in the sign of the smooth ORD curves.

Finally, dehydration of the hydrogenolysis products (VII) with thionyl chloride led to a hydrocarbon (XIII) with an 8(20) double bond and a specific rotation opposite in sign to the rotation of labd-8(20)-ene (XIV) (Table 1).

A mass-spectrometric analysis of vulgarol performed in comparison with that of labd-13-one-8α,15-diol confirmed the relationship of these two substances. Thus, the mass spectrum of vulgarol (Fig. 1) is characterized by the presence of a weak peak of the molecular ion, the fragmentation of which shows the presence of two hydroxy groups. Two molecules of water are eliminated in two directions: M – (18 + 15 + 18) [m/e 308 → 290 → 275 → 257] and M – (18 + 18 + 15) [m/e 308 → 290 → 272 → 257]. The 275 → 257 transition is confirmed by a metastable peak with m/e 240.5 (calculated, 240.2). Similar fragmentation is observed in the spectrum of labdene-8α, 15-diol (IV). Moreover, in the region of mass numbers relating to the fragmentation of the bicyclic

Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 722-728, November-December, 1975. Original article submitted October 25, 1974.