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CHEMICAL STUDY OF *Petasites albus*

U. K. Bagirova,[1] E. I. Mamedov,[1] and S. V. Serkerov[2]*

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A new compound was isolated pure by column chromatography of the acetone extract of Petasites albus *roots. Its structure was established as 5-isopropenyl-3-methyl-7-carboxybenzofuran (**1**) based on physicochemical and spectral (IR, PMR, ^{13}C NMR, ^{13}C DEPT 135) data.*

Keywords: *Petasites albus*, Asteraceae, sesquiterpenes.

In continuation of the chemical study of plants from the family Asteraceae growing in Azerbaijan, we investigated roots of *Petasites albus* (L.) Gaertn. (white butterbur) collected at the end of vegetation (November 2009) near the village Sebetkechmez, Kedabek Region, Azerbaijan Republic.

Chromatography of the total extracted substances obtained by acetone extraction (3×) of *P. albus* roots isolated pure crystalline **1**, R_f 0.49 (hexane), $C_{13}H_{12}O_3$, mp 128–130°C.

The IR spectrum contained characteristic frequencies bands for a carboxylic carbonyl and benzene C=C (broad overall band with a maximum at 1640 cm^{-1}) and strong absorption bands in the fingerprint region (800, 840, 905, 1160, 1280, 1300) indicating the presence of a carboxyl and benzene ring [1, 2]. The strong band at 905 was consistent with a methylene double bond in the structure [3].

The NMR spectrum taken with full proton decoupling exhibited 13 singlets characteristic of 13 C atoms in the basic structure of the compound. Of these, those with chemical shifts 17.5 and 31.5 ppm belonged to two methyls on a double bond; 98.0, 103.0, 113.0, and 124.0, to protonated olefinic C atoms; 116.5, 123.0, 133.0, 151.0, 158.5, and 159.0, to unprotonated olefinic C atoms; and 162.0, to a carboxyl C atom. The correctness of the assignments in the ^{13}C NMR spectrum was confirmed by the ^{13}C DEPT 135 spectrum, where resonances of two methyl C atoms at 17.5 and 31.5 ppm, three (98.0, 103.0, 124.0) protonated olefinic C atoms, and one (113.0) methylene double bond were found.

A comparison of the data given above with the literature, especially with physicochemical and spectral data of compounds obtained from representatives of the genus *Petasites* Milli [4, 5], led to the conclusion that the studied compound was new. We called it petalbusin.

The PMR spectrum of petalbusin exhibited eight singlets: two resonances with an area of 3H and six singlets with an area of 1H. Thus, resonances at 3.10 and 2.70 ppm provided evidence that petalbusin contained two vinyl methyls. The chemical shifts of these resonances were slightly lower than that of ordinary vinyl methyls. This was apparently due to the presence in the molecule of a more conjugated system such as a benzene ring condensed with a furan ring.

Highly oxygenated sesquiterpenes, mainly containing a furan ring, and sesquiterpene lactones of the eremophilane type, for example, furanoeremophilane, petasalbin, 9α-hydroxyfuroeremophilane, furanopetasol, furanopetasin, albopetasol, etc., were isolated from roots of species from the genus *Petasites* [5]. The furan ring in all these compounds contains a methyl group. It is possible from a biogenesis viewpoint that one of the methyls (2.7 ppm) in petalbusin is also located on the furan ring (in the β-position to the furan oxygen). The ^{13}C DEPT 135 spectrum shows 1H singlets at 5.20 and 5.70 ppm that belong to two protons of a methylene double bond (=CH_2).

Resonances of isolated (non-conjugated) exomethylenes are known to be located in PMR spectra at 4.8–5.2 ppm [6]. The chemical shifts of protons on a methylene double bond undergo a paramagnetic shift and are observed at comparatively weak field if conjugation is present or a hydroxy or epoxy group is located in a position vicinal to it. This is seen in a hydroxylactone (5.44 and 5.54) [7], badkhysinin (5.40 and 5.55) [8], oopodin (5.30 and 5.45) [9], etc. [3].

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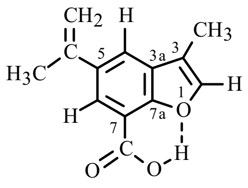
1) Gyanja State University, Gyanja, Azerbaijan; 2) Institute of Botany, National Academy of Sciences, Baku, Azerbaijan, e-mail: s.serkerov@mail.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 354–355, May–June, 2011. Original article submitted November 11, 2010.

The above examples show that the 1H resonances (at 5.20 and 5.70 ppm) in the PMR spectrum had chemical shifts that corresponded to methylene protons of a double bond that were conjugated to a double bond. Three of the four remaining 1H singlets (6.80, 6.90, and 8.15) belonged to three olefinic protons (two of a benzene ring and one of a furan ring). A 1H resonance (12.70) characterized the carboxylic acid (–COOH).

Thus, a summary of the data at this stage of the study could have assigned one of two structures (**1** or **2**) to petalbusin.



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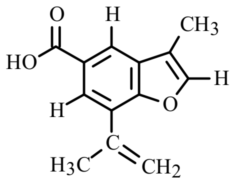

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The preferred structure was selected based on the PMR spectrum taken in CCl_4. The resonance of the carboxylic proton changed little (12.25) upon dilution. This indicated that an intramolecular H-bond was present [10, 11] between the carboxylic hydroxyl and the furan oxygen. Therefore, petalbusin had the structure 5-isopropenyl-3-methyl-7-carboxybenzofuran (**1**).

EXPERIMENTAL

General Comments. All solvents were freshly distilled. The purity of compounds was established by chromatography on UV-254 plates using hexane. IR spectra were recorded in mineral oil on a UR-20 spectrophotometer. PMR and ^{13}C NMR spectra were taken in deuterated acetone on a Bruker spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts are given on the δ-scale with TMS internal standard. Melting points were determined on a Boetius stage.

Extraction of Plant Material. Ground air-dried roots of *P. albus* (400 g) were extracted (3×, each time for 3 d) with acetone. The acetone was filtered and distilled off to afford total extracted substances (18 g, 4.5% yield).

Isolation of Petalbusin. Total extracted substances (18.0 g) were chromatographed over a column of deactivated Al_2O_3 (h = 62, d = 2.5 cm, Al_2O_3 neutral). The volume of each fraction was 100 mL. The column was eluted by hexane (26 fractions); hexane-benzene (2:1, two fractions; 1:1, five fractions; 1:3, four fractions), benzene (eight fractions), and $CHCl_3$. Fractions 1–11 that were eluted by hexane afforded a crystalline compound (from hexane) that was recrystallized from aqueous EtOH to give a compound of formula $C_{13}H_{12}O_3$, mp 128–130°C. IR spectrum (ν_{max}, cm^{-1}): 1640, 1300, 1280, 1160, 905, 840, 800. PMR spectrum (δ, ppm): 2.70 (3H, s, CH_3–C=), 3.10 (3H, s, CH_3–C=), 5.20 (1H, s) and 5.70 (1H, s, =CH_2), 6.80 (1H, s, –CH=), 6.90 (1H, s, –CH=), 8.15 (1H, s, –CH=) and 12.6 (1H, s, –COOH).

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