Chemistry of Natural Compounds, Vol. 38, No. 4, 2002

HAUTRIWAIC ACID FROM *Pulicaria salviifolia*

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UDC 547.91:547.595.9

A diterpene acid was isolated from the aerial part of Pulicaria salviifolia. *Spectral data and chemical transformations identify it as hautriwaic acid.*

Key words: *Pulicaria salviifolia*, diterpenoids, hautriwaic acid.

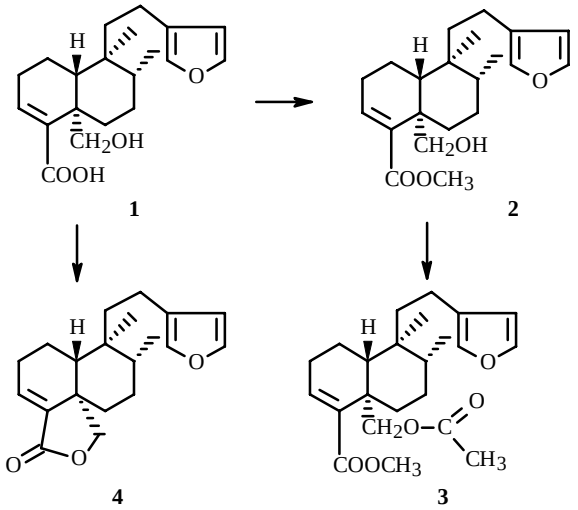
In continuation of the study of diterpenoids from the aerial part of *Pulicaria salviifolia* Bgl in Mem., sage-leafed fleabane, we isolated **1**, $C_{20}H_{28}O_4$, mp 179.5-180°C, by column chromatography of the total extracts of material collected at the start of fruiting in highlands of the Angren region of Tashkent district [1, 2].

The IR spectrum of **1** contains absorption bands (cm^{-1}) characteristic of hydroxyl (3180), carboxyl (2690 br.), carboxylic acid conjugated to a double bond (1660), and a furan ring (1590, 1540). The compound is very soluble in aqueous base.

The PMR spectrum of **1** has signals (δ, ppm, J/Hz): 0.72 (3H, d, J = 6, secondary methyl), 0.76 (3H, s, tertiary methyl), 3.95 (1H, d, J = 10.0) and 4.35 (1H, d, J = 10.0) (hydroxymethylene, AB system), and 1H broadened singlets at 6.30, 7.35, and 7.45 ppm for the furan ring. In addition, a broad 1H singlet at 6.85 ppm is seen for an olefinic proton conjugated to a carboxyl, the signal of which is found as a 1H broadened singlet at 9.80 ppm.

The spectral and chemical data indicate that **1** is hautriwaic acid, which was isolated earlier from *Dodonea viscosa* [3].

We prepared several derivatives that have been described previously [3] for convincing identification. Methylation of **1** by diazomethane in ether gave **2**, $C_{21}H_{30}O_4$, the PMR spectrum of which exhibits a 3H singlet at 3.70 ppm for the methoxycarbonyl protons in addition to other signals.



Acetylation of **2** by acetic anhydride in pyridine forms the acetate of the methyl ester of composition $C_{23}H_{32}O_5$ (**3**). The PMR spectrum of **3** contains a 3H singlet at 1.95 ppm. Protons of the methylene group appear in the spectrum of **3** at 4.30 and 4.55 ppm with acylation effects of 0.4 and 0.2 ppm, respectively.

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 0009-3130/02/3804-0326$27.00

Acetylation of **1** by acetic anhydride in pyridine gives the diterpenoid lactone $C_{20}H_{26}O_3$ (**4**), mp 117-118°C. The IR spectrum of **4** has an absorption band at 1765 cm^{-1}, typical of a lactone carbonyl.

It should be noted that the PMR spectrum of **4** exhibits a diamagnetic shift for the signals of the secondary and tertiary methyls compared with the starting compounds. They appear at 0.35 (3H, s) and 0.60 ppm (3H, d, J = 6.0 Hz), respectively.

A comparison of the physicochemical constants and spectral data of **1**-**4** indicates that **1** is hautriwaic acid [3]. This acid is found for the first time in plants of Central Asia.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer (KBr pellets); PMR, on a Tesla BS-567A/100 MHz instrument ($CDCl_3$, 0 = HMDS, δ). TLC monitoring was performed on Silufol (Chemarol) plates using hexane—ethylacetate (4:1) and chloroform—ethylacetate (4:1). The developer was vanillin in conc. H_2SO_4 (1% solution).

Isolation of Hautriwaic Acid (1). The air-dried aerial part of *Pulicaria salviifolia* (2 kg) collected during fruiting (September 1991) was extracted with $CHCl_3$ (5×4 L). The condensed extract was dissolved in ethanol, diluted with water (1:1), and left overnight. A precipitate formed and was removed. The aqueous ethanol solution was extracted repeatedly with ethylacetate. The solvent was distilled off. The resulting total extracted compounds (25.0 g) were placed on a column (3×180 cm) packed with silica gel (KSK) in a 1:15 ratio and eluted by chloroform—ethylacetate (9:1) with a gradually increasing concentration of ethylacetate. The 7:1 (chloroform—ethylacetate) fraction afforded hautriwaic acid, $C_{20}H_{28}O_4$, mp 179.5-180°C, yield 2 g, UV spectrum (λ_{max}) 220 nm (log ε 3.95).

Methylester of Hautriwaic Acid (2). Compound **1** (100 mg) was dissolved in diethyl ether and treated with diazomethane in the same solvent. The reaction mixture was left for 1 h and produced the methyl ester of hautriwaic acid, $C_{21}H_{30}O_4$ (**2**). PMR spectrum: 3.70 (s, 3H, OCH_3).

Acetate of the Methyl Ester of Hautriwaic Acid (3). Compound **2** (100 mg) was dissolved in pyridine (3 mL), treated with acetic anhydride (1 mL), and left overnight. The reaction product was diluted with water and treated with ethylacetate (3×40 mL). The ethylacetate extract was washed with H_2SO_4 (5%) and water and dried over Na_2SO_4. The solvent was distilled off to give the acetyl derivative, $C_{23}H_{32}O_5$ (**3**). The PMR spectrum contains a singlet at 1.95 ppm (3H, OCO–CH_3).

Preparation of Lactone 4. Hautriwaic acid (35 mg) was dissolved in pyridine, treated with acetic anhydride (2 mL), and left overnight. The reaction product was isolated as described above to give lactone $C_{20}H_{26}O_3$, mp 119-120°C.

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