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A New Diglycoside of Diterpene from *Ageratina vacciniaefolia*

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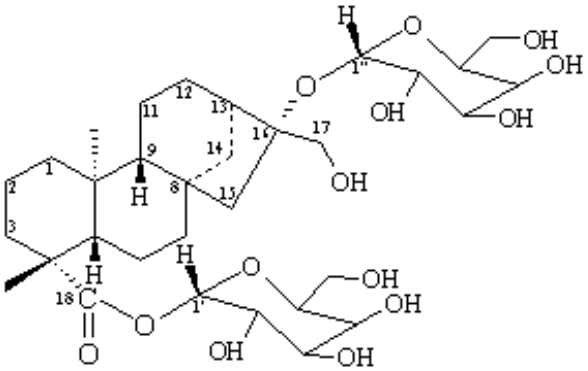

From leaves and flowers of *Ageratina vacciniaefolia* [1-7] we have isolated several compounds: a flavonoid, a diterpene [8] and a new compound identified as b-D-glucopyranosil ester of (-)17-(b-glucopiranosyloxyl)-16-hydroxy-kauran-19-oic acid (see the formula). The structure was established by using ^{1}HNMR, ^{13}CNMR, COSY, NOESY and HMBC spectroscopic techniques (Table 1) [1,7].

Table 1. The assignment of the NMR data [2-6].

No. C	Type of C	d -ppm
19	-COO	178.2
1*	CH(anomeric)	98.5
1**	CH(anomeric)	95.6
16	C-O	91.4
	CH –O	78.7
	CH -O	78.7
	CH -O	78.3
	CH -O	77.7
	CH-O	75.2
	CH -O	74.1
	CH -O	71.4
	CH -O	71.1
17	CH_2-O	63.6
	CH2OH	62.5
	CH2-O	62.4

9	CH	58.5
5	CH	57.3
15	CH_2	51.4
solv.	solv.	49.8
8	C	46.0
4	C	45.1
13	CH	44.2
7	CH_2	43.1
1	CH_2	41.8
10	C	40.9
3	CH_2	39.1
14	CH_2	37.6
18	CH_3	29.1
12	CH_2	26.8
6	CH_2	23.2
11	CH_2	20.1
2	CH_2	19.7
20	CH_3	16.4

The ^{13}CNMR spectrum showed totally 32 signals, 12 of them at ca. 62-99 ppm which are characteristic of glycoside. The rest 20 signals are attributed to the aglicone which is a compound of diterpene kaurane type, and the structure has been confirmed by both ^{13}CNMR and ^{1}HNMR spectra.

The signals from ^{1}HNMR at d 4.48 ppm (d, *J*=7.2 Hz) was assigned to the anomeric proton, whcih has a direct correlation with C of d 98.45 ppm indicating a b-glycoside; while ^{1}HNMR signals appear at d 5.434 ppm (d, *J*= 7.2 Hz) coupling directly with C at d 95.56 ppm can be attributed to a b-glucose ester. Furthermore, the absence of signals to vinilic protons and the absence of signals to C9 and C15 connected to oxygen, similar to those in the other compound [8], indicate that this aglicone compound is a Kaurane derivative. The signal from ^{13}CNMR spectrum at d 63.60 ppm showed a -CH_2OH connected to C17 which was confirmed by correlation observed on HMBC and NOESY spectra. A signal at d 91.55 ppm indicating a glucose connected to C16 is confirmed by a long range correlation on HMBC spectrum. An enzymatic hydrolysis of this compound with b-glucosidase also confirmed the structure purposed.

In summary, this compound was identified as b-D-glucopyranosil ester of (-)17-(b-glucopiranosyloxyl)-16-hydroxykauran-19-oic acid by using HNMR and ^{13}CNMR spectra analysis and enzymatic hydrolysis with b-glucosidase [7].

The ethanolic extract from leaves and flowers of *A. vacciniaefolia* yielded white crystals after column chromatography and eluted with CH_2Cl_2, EtOAc and mixtures of these solvents. The compound was purified further by column chromatography on RP-18 eluted with MeOH-H_2O (2:1).

M.p. 198ºC.

$[a]^{20}_{D}$ = -52.5 (0.0043 MeOH).

DCIMS [isobutane] m/z: 499; 481; 463; 419; 392; 391; 361; 319; 273; 163; 145 (100%); 127.

^{1}HNMR (360 MHz, CD_3OD): d in ppm, 0.96 (s, 3H, CH_3); 1.20 (s, 3H, CH_3);1.45 (m, 1H); 1.85 (m, 1H); 2.25 (m, 1H); 3.18 (m, 1H); 3.33 (m, 1H); 3.37 (m, 2H); 3.7 (dd, 1H, *J*=12.3Hz); 3.8 (dd, 1H, *J*=12.2 Hz); 4.48 (d, 1H, *J*=7.2 Hz, anomeric proton); 5.43 (d, 1H *J*=7.2, anomeric proton).

^{13}CNMR (90.5 MHz, CD_3OD): d 16.38 (-CH_3, C); 19.71; 29.05 (-CH_3, C); 20.12; 25.17; 26.82; 37.62; 39.05; 40.92; 41.84; 43.07; 44.21; 45.08; 45.97; 51.40; 57.29; 58.54; 62.40; 62.52 (-CH_2OH); 63.60 (-CH_2-O-); 71.10; 71.42; 74.08; 75.18; 77.73; 78.29; 78.64 (2C); 91.55; 95.56; 98.45; 178.16 (-COO, C19). For details, see the following table (Table 1).

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References

1. Hasan, C. M., Healey, T. M. and Waterman P. T. *Phytochemistry* **1982**, *21*, 1365.
2. Demetzos, C., Harvala, C., Phillianos, S. Manol Skaltsounis, A. *J. Nat. Prod.* **1991**, *53*, 1365.
3. Torrenegra, R., Pedrozo, J., Robles, J., Waibel, R. and Achenbach, H. *Phytochemistry* **1992**, *31*, 2415.
4. Konzi, S. A. and McChesney, J. D. *J. Nat. Prod.* **1991**, *54*, 483.
5. Aranda, G., El Kortbi, M. S., Lallemand, J. Y. *Tetrahedron* **1991**, *47*, 8339.
6. Konig, W. A., Lutz, S. and Wenz, G. *Angew. Chem.* **1988**, *100*, 989.
7. Breitmaier Eberhard, *Structure Elucidation by NMR in Organic Chemistry*, John Wiley & Sons, New York (1993).
8. Torrenegra, R., Robles, J., Pedrozo, J., Pescador B. *Molecules* **1999**, *4,* M92.

Sample Availability: Available from the authors and from MDPI. MDPI 16329.