

## COMPOSITE CONSTITUENTS: NEW MIGRATED GAMMACERANE TRITERPENOIDS FROM ROOTS OF *PICRIS HIERACIOIDES* SUBSP. *JAPONICA*

Kenji Shiojima, Kazuo Masuda, Yuko Ooishi, Hideki Suzuki and Hiroyuki Ageta\*  
Showa College of Pharmaceutical Sciences, 5-1-8 Tsurumaki, Setagaya-ku, Tokyo 154, JAPAN

**SUMMARY:** Migrated gammacerane triterpenoids, named pichierenyl acetate (**1**) and isopichierenyl acetate (**2**), were isolated from the fresh roots of *Picris hieracioides* subsp. *japonica*, Compositae. By spectral and chemical methods, the structures of **1** and **2** were established as the members of migrated gammacerane series with a  $\Delta^{9(11)}$  and a  $\Delta^8$  double bond respectively.

Recently we reported three new gammacer-16-ene derivatives, gammacer-16-en-3 $\beta$ -yl acetate (**3**) and its corresponding 3 $\beta$ - and 3 $\alpha$ -ols from the fresh roots of *Picris hieracioides* LINNÉ subsp. *japonica* (THUNB.) KRYLOV. (Kôzorina in Japanese, Compositae),<sup>1</sup> in which we also described the presence of migrated gammacerane triterpenoids. By GC analysis,<sup>2</sup> two unknown small peaks ( $R_{tR}$  5.16 and 4.88) were detected in one of the acetate fractions and the two novel triterpenoid acetates, named pichierenyl acetate (**1**) and isopichierenyl acetate (**2**), which belong to the migrated gammacerane series, were isolated by 20%-AgNO<sub>3</sub>-Si gel CC and HPLC (C<sub>18</sub>, CH<sub>3</sub>CN). We report here the structures of these compounds.

Pichierenyl acetate (**1**): 0.0009% (an estimated yield of the dried roots),  $R_{tR}$  5.16, mp 272.5-273.5°C,  $[\alpha]_D^{23}$  -31.2° (CHCl<sub>3</sub>, c=0.3), M<sup>+</sup> m/z 468.4004 (C<sub>32</sub>H<sub>52</sub>O<sub>2</sub>), IR  $\nu_{max}^{KBr}$  cm<sup>-1</sup>: 1734, 1248, 1023, 817, 797. Isopichierenyl acetate (**2**): 0.0002%,  $R_{tR}$  4.88, mp 248.5-249.5°C,  $[\alpha]_D^{23}$  -2.6° (CHCl<sub>3</sub>, c=0.1), M<sup>+</sup> m/z 468.3935 (C<sub>32</sub>H<sub>52</sub>O<sub>2</sub>), IR  $\nu_{max}^{KBr}$  cm<sup>-1</sup>: 1730, 1247, 1020. The EI-MS of **1** (rel. int. in parentheses) and **2** (rel. int. in square brackets) showed the same major fragments (except for relative intensities): m/z 315 (a), 255 (a'), 301(b), 241 (b'), 289 (c) and 229 (c'). These fragments are observed characteristically in  $\Delta^7$ -,  $\Delta^8$ - and  $\Delta^{9(11)}$ -3 $\beta$ -yl acetates of fernane

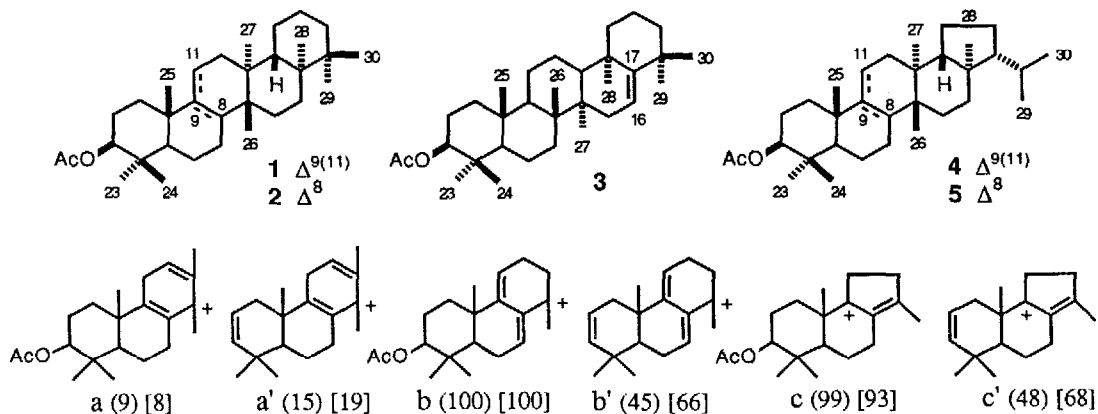


Table 1.  $^1\text{H}$ -Chemical Shifts ( $\delta$ ) in  $\text{CDCl}_3$  Solution on JEOL GX 270 at 270 MHz

	H-23	H-24	H-25	H-26	H-27	H-28	H-29	H-30	H-3 $\alpha$	H-11
1	0.841	0.939	1.087	0.701	0.768	1.032	0.971	0.788	4.478dd (6.6,9.3)	5.305ddd (2.2,2.5,5.3)
2	0.877	0.870	0.972	0.956	0.747	1.042	0.983	0.776	4.492dd (6.6,9.3)	
4	0.844	0.940	1.084	0.728	0.803	0.757	0.824d (6.4)	0.889d (6.4)	4.482dd (6.6,9.3)	5.294ddd (2.4,2.9,4.6)
5	0.875	0.875	0.970	0.951	0.752	0.767	0.823d (6.4)	0.888d (6.4)	4.496dd (6.6,9.3)	

Coupling constants are shown in parentheses. An acetyl methyl signal for **1** appeared at  $\delta$  2.047, for **2** at  $\delta$  2.051, for **4** at  $\delta$  2.051 and for **5** at  $\delta$  2.049. Assignments were confirmed by  $\text{CDCl}_3$ - $\text{C}_6\text{D}_6$  solvent and lanthanide shifts.

Table 2.  $^{13}\text{C}$ -Chemical Shifts ( $\delta$ ) in  $\text{CDCl}_3$  Solution on JEOL GX 270 at 68 MHz

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
1	39.1	24.7	81.1	37.6	44.6	17.4	19.0	40.3	150.2	37.3	116.7	37.2	37.2	38.2	28.1	37.6
4	39.0	24.7	81.1	37.7	44.5	18.1	19.6	40.0	150.8	37.7	116.5	36.8	36.8	38.2	29.3	36.2

	C-17	C-18	C-19	C-20	C-21	C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30	acetyl carbons
1	38.2	41.2	23.3	21.8	27.9	39.3	27.4	16.2	25.3	15.2	16.5	23.0	16.4	25.3	21.3 171.0
4	43.0	52.0	20.2	28.3	59.7	30.8	27.4	16.2	25.1	15.8	15.4	14.0	22.2	23.0	21.3 171.1

Chemical shifts of methyl groups were confirmed by proton selective decoupling method.

and multiflorane skeletons. Of the eight tertiary methyl proton signals observed in the  $^1\text{H}$ -NMR of **1** and **2** (Table 1), three (H-23~25) were very similar to those of **4** and **5** respectively.<sup>3</sup> The other five methyl signals (H-26~30) did not coincide with those of multiflor-9(11)-ene and multiflor-8-ene.<sup>4</sup> Olefinic proton of **1** showed almost the same splitting pattern and chemical shift as that of **4**, whereas **2** showed no olefinic proton signal. The identity of  $^{13}\text{C}$ -chemical shifts (Table 2) of the A and B ring moiety in **1** with those of **4** also indicates that the left counterpart of **1** is the same as that of **4**. In addition,  $R_{\text{FS}}$  of **1** and **2** on GC were not identical with any of other known  $\Delta^9(11)$  and  $\Delta^8$  triterpenoid  $3\beta$ -yl acetates. On the basis of this and biogenetic indication (this plant contains **3**), **1** and **2** are presumed to be migrated gammacerane triterpenoids with a  $\Delta^9(11)$  and a  $\Delta^8$  double bond in the molecule respectively.

The structure of **1** and **2** were confirmed by the following acid induced rearrangement experiments.<sup>5</sup> Compound **1** was treated with  $1\text{N-H}_2\text{SO}_4$ - $\text{AcOH-C}_6\text{H}_6$  at  $20^\circ\text{C}$  for 15 hrs to give **2** in a good yield and **2** was also obtained from **3** in the same way. Thus pichierenyl acetate (**1**) and isopichierenyl acetate (**2**) were found to be examples of  $\Delta^9(11)$  and  $\Delta^8$  triterpenoids of the migrated gammacerane series.<sup>6</sup>

#### REFERENCES AND NOTES

1. K. Shiojima, K. Masuda, T. Lin, H. Suzuki and H. Ageta, *Tetrahedron Lett.*, in press.
2. GC was run on a Hitachi 163 with chromosorb G HP coated with SE-30 (1.4%) at  $260^\circ\text{C}$  in a flow of nitrogen. Cholestane was used as an internal reference; its retention time was set at 3.0 min.
3. H. Ageta and T. Ageta, *Chem. Pharm. Bull.*, **32**, 369 (1984). The MS and  $^1\text{H}$ -NMR of **5** was taken with a sample derived from **4**.
4. H. Ageta and Y. Arai, *Phytochemistry*, **22**, 1801 (1983).
5. H. Ageta, K. Shiojima and Y. Arai, *Chem. Pharm. Bull.*, **35**, 2705 (1987).
6. Only recently, swertanone was reported as a  $\Delta^7$  compound. A. K. Chakravarty, B. Das, S. C. Pakrashi, D. R. McPhail and A. T. McPhail, *J. Chem. Soc. Chem. Commun.*, **1989**, 438.

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