COMPOSITE CONSTITUENT: NOVEL TRITERPENOID, IXERENOL, FROM AERIAL PARTS OF IXERIS CHINENSIS

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A novel triterpenoid, ixerenol (1), has been isolated together with twelve known triterpenoid alcohols as acetates; its structure was determined by extensive spectroscopic analyses.

KEYWORDS Ixeris chinensis; triterpenoid; ixerenol; Compositae

In the previous communication, 1) we reported the structure of a novel triterpenoid, 17-epi-lupenyl acetate, isolated from the acetate fraction of dried aerial parts of Ixeris chinensis (Thunb.) Nakai. Further investigation of the alcohol fraction of the same source resulted in the isolation of a novel triterpenoid, named ixerenol (1), together with twelve known compounds, lupeol, 2) germanicol, 2) β-amyrin, 2) taraxerol, 3) taraxasterol, 2) ψ-taraxasterol, 2) α-amyrin, 2) bauerenol, 2) tirucalla-7,21-dien-3β-ol, 4) butyrospermol, 5) cycloartenol, 6) and 3β-hydroxytaraxaster-20-en-30-ol, 7) as acetates. In this paper, we wish to report the structure elucidation of compound 1 on the basis of spectral evidence.

The hexane extract of dried materials was chromatographed on silica gel to give the alcohol fraction (0.5 g, 0.11 % of the dried materials) as benzene eluate. This fraction was acetylated with Ac2O-pyridine, and the mixture was chromatographed repeatedly on 20% AgNO3-impregnated silica gel, followed by prep. HPLC [C-18 reverse phase, CH3CN–CHCl3 (9:1)] to give ixerenyl acetate (1a), mp 158–160 °C, [α]D +39.5° (CHCl3, c=0.1). The MS of 1a showed the molecular ion at m/z 468.3959 (C32H52O2), and many significant fragment ions at m/z (rel. int.): 453 (9, M+–CH3), 425 (5, a), 408 (32, M+–AcOH), 393 (25, M+–CH3–AcOH), 365 (4, a–AcOH), 262 (25, b), 249 (12, c), 218 (31, d, e), 204 (61, f, g), 202 (24, b–AcOH), 189 (100, h, i), and 135 (35, j) (Chart 1). This fragmentation pattern indicated that the structure of rings A, B and C of 1a was essentially identical with those of lupenyl acetate (2a). 8) The 1H-NMR spectrum of 1a showed the presence of seven tertiary methyl groups, exocyclic methylene group, and 3β-acetoxyl group in the molecule. The 1H- and 13C signals of rings A, B and C (except C-12 and C-13 in 1a) were very similar to those of 2a, 1) suggesting the same structure. The analysis of 1H–1H COSY, HSQC, and HMBC spectra suggested that 1a had a methylene (C-18)
Fig. 1. Partial Structure of 1a by HMBC Spectrum

Fig. 2. Chem3D Plus Drawing and NOEs of 1a

Chart 1

Chart 2
between C-13 and C-19, a methine (C-16), and an exocyclic methylene (C-28) attached to C-17. The partial structure of 1a, shown by heavy lines in Fig. 1, was established by the HMBC spectrum. In addition, all methylene and methine carbons were correlated from the corresponding proton signals, confirmed by the $^1$H-$^1$H COSY spectrum with the signals of proton(s) attached to the neighboring carbon(s).$^9$ Useful information for stereochemistry of 1a was obtained by the NOE spectrometry. That is, cross-peaks were observed between H-24 and 25, H-25 and 26, H-26 and 13$\beta$, H-13$\beta$ and 30, H-15$\beta$ and 30, H-15$\beta$ and 22$\beta$, H-21$\beta$ and 30, H-22$\beta$ and 30; H-9$\alpha$ and 27, H-27 and 16$\alpha$, H-16$\alpha$ and 19$\alpha$, H-16$\alpha$ and 28a, H-19$\alpha$ and 29, and H-22$\alpha$ and 28b (Fig. 2 and Note 10). The D and E ring juncture was the cis configuration of 16$\alpha$-H and 19$\alpha$-H. Therefore, 1a was a new type of skeleton, as shown in Chart 2.

It is noteworthy to mention that a new skeletal triterpenoid having three rings (C, D and E) side by side was isolated from a natural source. Biogenetically, we estimate that cyclization of squalene oxide gives the germanane cation, whose C-17 and C-18 bond open followed by recyclization to afford 1 (Chart 2).

**ACKNOWLEDGEMENT** The authors are indebted to Mr. Yôichi Takase of this College for MS measurements.

**REFERENCES AND NOTES**


10) $^1$H-NMR (CDCl$_3$, 500MHz, $\delta$H, $\delta$H$_{3}$ for methylene signals): 1.02:1.71 (H-1), 1.63:1.63 (H-2), 4.481 (dd,$J=5.8$, 10.9Hz, H-3), 0.81 (H-5), 1.50:1.37 (H-6), 1.37:1.37 (H-7), 1.39 (H-9), 1.47:1.28 (H-11), 1.00; 1.33 (H-9), 1.81 (H-13), 0.85:1.79 (H-15), 2.50 (H-16), 1.31:1.48 (H-18), 1.46 (H-19), 1.26:1.45 (H-21), 2.02:2.31 (H-22), 0.844 (H-23), 0.838 (H-24), 0.876 (H-25), 0.981 (H-26), 0.954 (H-27), 4.576:4.579 (H-28), 0.892 (H-29), 1.087 (H-30), 2.044 (-OCOCH$_3$).

$^{13}$C-NMR (CDCl$_3$, 125MHz , $\delta$) 38.62 (C-1), 23.71 (C-2), 80.97 (C-3), 37.84 (C-4), 55.66 (C-5), 18.06 (C-6), 33.74 (C-7), 40.77 (C-8), 51.24 (C-9), 37.23 (C-10), 21.37 (C-11), 30.25 (C-12), 33.17 (C-13), 40.90 (C-14), 36.45 (C-15), 40.94 (C-16), 155.44 (C-17), 29.58 (C-18), 43.30 (C-19), 33.77 (C-20), 44.18 (C-21), 28.66 (C-22), 27.92 (C-23), 16.49 (C-24), 16.56 (C-25), 15.56 (C-26), 14.30 (C-27), 106.47 (C-28), 32.59 (C-29), 25.83 (C-30), 21.34 (-OCOCH$_3$), 171.04 (-OCOCH$_3$).

(Received October 28, 1994; accepted November 26, 1994)