[Chem. Pharm. Bull. 21(6)1395—1396(1973)]

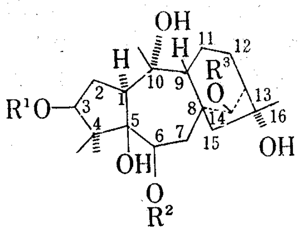
UDC 547.597.04

Correlation of Lyoniol-A (Lyoniatoxin) with Grayanotoxin-I

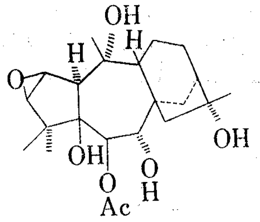
Lyoniol-A, the toxic principle of *Lyonia ovalifolia* var. *elliptica*, and grayanotoxin-I, the main toxic compound of *Leucothoe grayana*, were assumed to have the same carbon skeleton, because they have very closely relationship between plant sources, similar biological actions, similar chemical reactions and similar physical data of their derivatives.[1] Besides the structure of grayanotoxin-I (I) was determined by X-ray chrystallography.[2] Thus, we attempted to correlate lyoniol-A (II) with grayanotoxin-I (G-I).

7,16-Di-O-acetyldihydrolyoniol-B[3] (IV) was treated with chromic acid in pyridine to yield a diketone, 3,6-dioxo-7,16-diacetoxy-5,10-dihydroxygrayanane (V). Colorless needles (from benzene), mp 183—185°. *Anal.* Calcd. for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.68; H, 7.80 IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3480, 1740, 1730, 1710. The reduction of V with metallic calcium in liquid ammonia[4] resulted in the removal of the acetoxyl group adjacent to the C-6-oxogroup. This crude reduction product was hydrolysed with 5% methanolic alkali and again oxidized the partially reduced oxogroup to 3,6-diketone (VI). Colorless needles (from ethyl acetate), mp 252—256° (decomp.). IR $_{\max}^{\text{KBr}}$ cm^{-1}: 3480, 1735, 1705. Mass spectrum (MS). Calcd. for $C_{20}H_{30}O_5$: 350. Found: 350 (M^+).

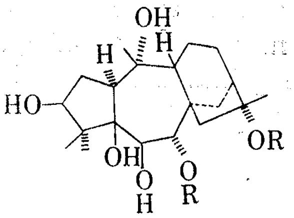
On the other hand benzoylation of G-I gave a mixture of 3-O-,[5] 3,6-di-O-[6] and 6-O-benzoate (VII). 6-O-Benzoate was separated from the mixture by alumina column chromatography. VII: Syrup. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3420, 1745, 1710, 1600. NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 0.90, 1.20, 1.37, 1.50 (each 3H, s), 2.44 (3H, s, $COCH_3$), 3.75 (1H br. d, C-3H), 4.90—5.30 (1H, m, C-6H), 5.80 (1H, s, C-14H), 7.30—8.20 (5H, m, aromatic proton). Acetylated VII (VIII) was partially hydrolysed with 1% methanolic potassium carbonate to yield 14-hydroxy-3-acetoxy-6-benzoyloxy derivative (IX). Colorless needles (from benzene), mp 243—245°. *Anal.* Calcd. for $C_{29}H_{40}O_8$: C, 67.42; H, 7.80. Found: C, 67.45; H, 7.51. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3420, 1740, 1710. The 14-hydroxyl group of IX was oxidised to carbonyl and then reduced by Wolff-Kishner method to methylene derivative. This crude product was again oxidised with chromic acid



	R¹	R²	R³
I	H	H	Ac
VII	H	Bz	Ac
VIII	Ac	Bz	Ac
IX	Ac	Bz	H

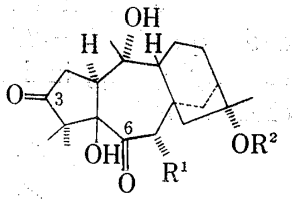


II



III : R=H

IV : R=Ac



	R¹	R²
V	OAc	Ac
VI	H	H

---

1) M. Yasue, T. Kato, and J. Sakakibara, *Chem. Pharm. Bull.* (Tokyo), **18**, 854, 2586 (1970); J. Sakakibara, K. Ikai, and M. Yasue, *ibid.*, **20**, 861 (1972).

2) P. Narayanan, M. Röhrl, K. Zechemister, and W. Hoppe, *Tetrahedron Letters*, **1970**, 3943.

3) T. Kato, J. Sakakibara, and M. Yasue, *Yakugaku Zasshi*, **91**, 1194 (1971).

4) J.H. Chapman, J. Elks, G.H. Phillipps, and L.J. Wyman, *J. Chem. Soc.*, **1956**, 4344.

5) H. Kakisawa, T. Kozima, M. Yanai, and K. Nakanishi, *Tetrahedron*, **21**, 3091 (1965).

6) Tsunematsu Takemoto, Nobushige Nishimoto, Haruo Meguri, and Kazuko Katayama, *Yakugaku Zasshi*, **78**, 112 (1958).

in pyridine to yield the corresponding diketone, 3,6-dioxo-5,10,16-trihydroxygrayanane. Colorless needles (from ethyl acetate), mp 254—259° (decomp.). *Anal.* Calcd. for $C_{20}H_{30}O_5$: C, 68.54; H, 8.63. Found: C, 68.15; H, 8.33. IR ν_{max}^{KBr} cm^{-1}: 3480, 1735, 1705. Mass Spectrum: 350 (M$^+$).

The final product was identified by IR and MS as VI, derived from lyoniol-A. Lyoniol-A, lyoniol-B and lyoniol-D were already correlated each other by chemical reactions.[1] So this experiments also confirmed the stereostructures of lyoniol-B and lyoniol-D.

Faculty of Pharmaceutical Sciences,
Nagoya City University
Tanabe-dori, Mizuho-ku, Nagoya

JINSAKU SAKAKIBARA
KATSUSHIGE IKAI
MASAITI YASUE

Received March 12, 1973

[Chem. Pharm. Bull.
21(6)1396—1397(1973)]

UDC 547.597.03.04

Application of Homonuclear INDOR Spectroscopy in Friedelin Type Triterpenes

The INDOR method in nuclear magnetic resonance (NMR) spectroscopy was first described by Baker[1] and its usefulness in the structure analyses of complex organic molecules has recently been demonstrated by Sciacovelli, *et al.*[2] and Ayres, *et al.*[3] We were interested in the application of this method to the assignment of methyl resonances of triterpenes and examined the spectra of 16β-acetoxyfriedelane (IIIa), mp 216—217°, and the 16α-epimer (IIIb), mp 182—183°.[4] These compounds had been obtained *via* the mono-ketone (II) from both pachysandiol-B (Ia) and pachysonol (Ib), isolated from *Pachysandra terminalis* SIEB. et ZUCC., and their structures were already established.[4]

The NMR spectra of IIIa and IIIb (Fig. 1 and 2) showed a triplet (J=9 Hz) at δ 5.22 and a quartet (J=7.5 and 8.5 Hz) at δ 5.19, respectively, due to the hydrogen geminal to the acetoxyl group, indicating that the D-ring in IIIa is in boat form while that in IIIb is in chair form.[5]

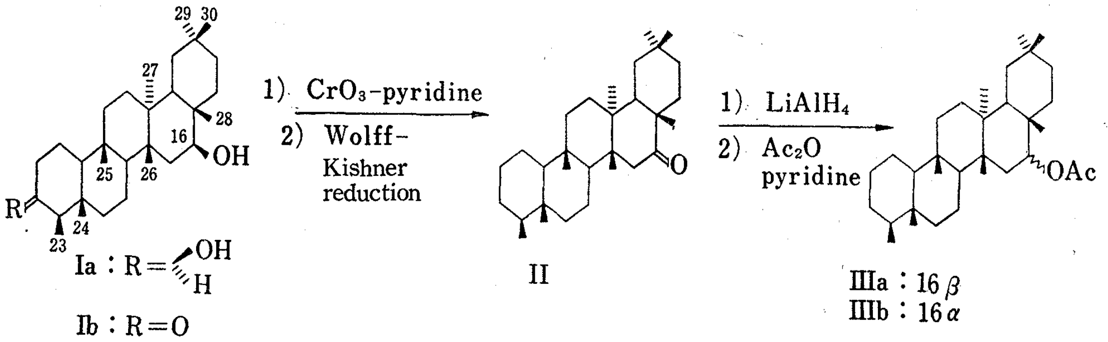


Chart 1

---

[1] E.B. Baker, *J. Chem. Phys.* **37**, 911 (1962).
[2] O. Sciacovelli, W. von Philipsborn, C. Amith, and D. Ginsburg, *Tetrahedron*, **26**, 4589 (1970).
[3] D.C. Ayres, J.A. Harris, P.N. Jenkins, and L. Phillips, *J. Chem. Soc.* (*Perkin I*), **1972**, 1343.
[4] T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, *Tetrahedron Letters*, **1971**, 1535; *idem*, *Chem. Pharm. Bull.* (Tokyo), in press.
[5] T. Kikuchi, M. Niwa, and N. Masaki, *Tetrahedron Letters*, **1972**, 5249.