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 $\nu_{\max}^{\mathrm{KBr}}$ $\mathrm{cm}^{-1}$: 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 16$\beta$-acetoxyfriedelane (IIIa), mp 216—217°, and the 16$\alpha$-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 $\delta$ 5.22 and a quartet ($J$=7.5 and 8.5 Hz) at $\delta$ 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]

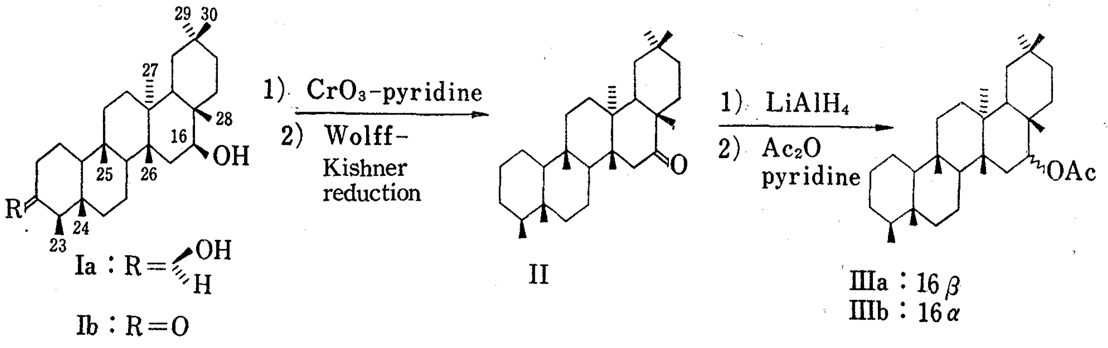

Chart 1

---

[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.

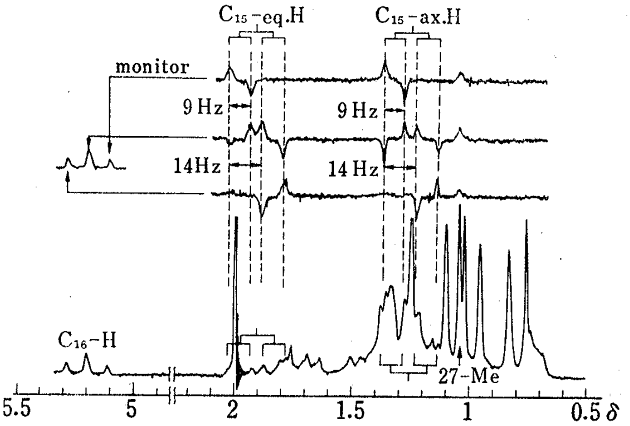

Fig. 1. 100 MHz Proton Spectrum of 16β-Acetoxyfriedelane (IIIa) in $CDCl_3$ and INDOR Spectra using Three Transitions of $C_{16}$-H as Monitor Lines (internal standard: TMS)

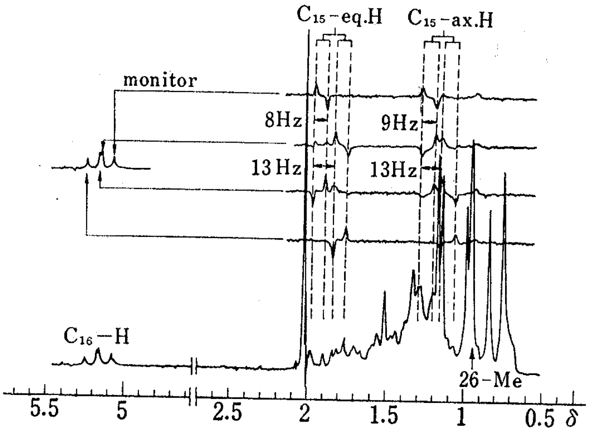

Fig. 2. 100 MHz Proton Spectrum of 16α-Acetoxyfriedelane (IIIb) in $CDCl_3$ and INDOR Spectra using Four Transitions of $C_{16}$-H as Monitor Lines (internal standard: TMS)

First we examined the INDOR spectra[6] of IIIa. As shown in Fig. 1, monitoring triplet lines for the 16-hydrogen at δ 5.22 gave two sets of INDOR signals around δ 1.90 and 1.24. The lower field signals may be ascribed to the 15-equatorial hydrogen and the higher field signals to the 15-axial one. In this experiment, there was observed a small peak at δ 1.04, which may be ascribed to the increment of signal intensity due to the so-called nuclear Overhauser effect (NOE). This was confirmed by irradiation at the methyl signal of δ 1.04, which gave 11% increment of signal intensity of the 16-hydrogen at δ 5.22. Accordingly, the signal at δ 1.04 could be assigned to the 27-methyl group.

Next the INDOR experiment was performed with the compound IIIb. Monitoring the quartet lines of 16-hydrogen geminal to the acetoxyl group revealed the INDOR signals for 15-hydrogens as illustrated in Fig. 2. There was also appeared a small peak at δ 0.96. Irradiation at this position, in turn, gave 13% NOE increment of the 16-hydrogen at δ 5.19. Thus the methyl signal at δ 0.96 was partly assigned to the 26-methyl group which is in 1,3-diaxial relation to the 16-hydrogen.

In conclusion, the INDOR method is very effective not only for the determination of signal position of hidden protons which are spin-coupled, but also for the qualitative detection of conventional NOE and therefore very useful in the stereochemical analyses of complex organic molecules.

*Faculty of Pharmaceutical*
*Sciences, Kyoto University*
*Yoshida-shimoadachi-cho,*
*Sakyo-ku, Kyoto*

Tohru Kikuchi
Tetsuro Shingu
Mineo Niwa
Toshio Yokoi

Received March 15, 1973

---

6) The proton NMR and INDOR spectra were measured in $CDCl_3$ solution using a Varian HA-100D Spectrometer which was modified for INDOR experiments according to the description by Jenkins and Phillips. See P.N. Jenkins and L. Phillips, *J. Phys.* (*E*), **4**, 530 (1972).