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Studies on the Constituents of Asclepiadaceae Plants. LXIV.[1)] The Structure Elucidation of Cynafogenin

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Cynafogenin (**1**) contains two distinct ester groups, acetate and benzoate, located at C-11 and C-12, respectively. The positions of the ester linkages were determined by an application of the long-range selective proton decoupling (LSPD) technique. Further, the aromatic carbons of benzoate and the methyl carbons at C-18 and C-19 were assigned.

Keywords——cynafogenin; *Cynanchum africanum*; Asclepiadaceae; long-range selective proton decoupling (LSPD) technique

In the previous paper, we reported the structures of two glycosides isolated from *Cynanchum africanum* R. Br. (Asclepiadaceae).[2)] The common aglycone, named cynafogenin (**1**), contains two distinct ester groups, acetate and benzoate, located at C-11 and C-12, but the exact position of each was unknown. Similar aglycones have been isolated from several Asclepiadaceae plants by Reichstein *et al.*[3)] and Tschesche *et al.*,[4)] and their structures were deduced on the basis of complicated chemical transformations. In this paper, we wish to describe the structural determination of **1** by analysis of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra.

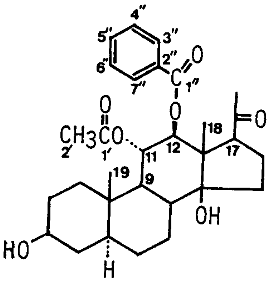

Chart 1

The long-range selective proton decoupling (LSPD) technique[5)] has made it possible to correlate the protons owing ester groups with their carbonyl carbons. When the proton signals at δ 5.72 (11-CH$_\beta$) and δ 1.78 (2′-Me: methyl protons of acetate) were weakly irradiated, the intensity of the carbon signal at δ 170.4 (C-1′) increased and the splitting was eliminated simultaneously (Fig. 1). Individual irradiation of the proton signals at δ 5.38 (12-CH$_\alpha$) and δ 8.33 (3′′, 7′′-CH: *ortho* protons of benzoate) increased the intensity of the carbon signal at δ 166.8 (C-1′′). Thus, the acetoxyl group was located at C-11 and the benzoyl group

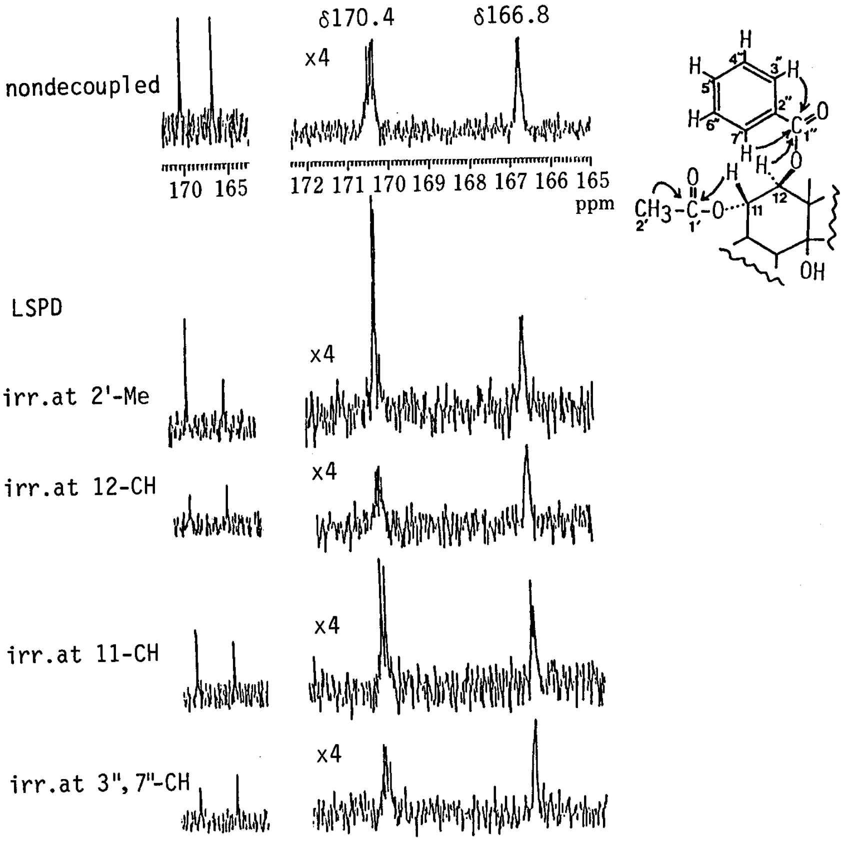

Fig. 1. Nondecoupled and LSPD Spectra

Table I. ^{13}C-NMR Chemical Shifts of **1** (δ in ppm)

C-1	38.3	C-11	71.7	C-1′	170.4
C-2	32.8	C-12	79.1	C-2′	21.4
C-3	69.9	C-13	55.0	C-1″	166.8
C-4	39.7	C-14	84.0	C-2″	130.2
C-5	45.1	C-15	33.9	C-3″	130.2
C-6	29.5[a)]	C-16	24.3	C-4″	129.2
C-7	28.5[a)]	C-17	58.5	C-5″	133.9
C-8	40.2	C-18	11.9	C-6″	129.2
C-9	50.2	C-19	12.5	C-7″	130.2
C-10	38.0	C-20	213.3		
		C-21	31.7		

a) May be interchangeable. Measured in C_5D_5N with tetramethylsilane as an internal standard.

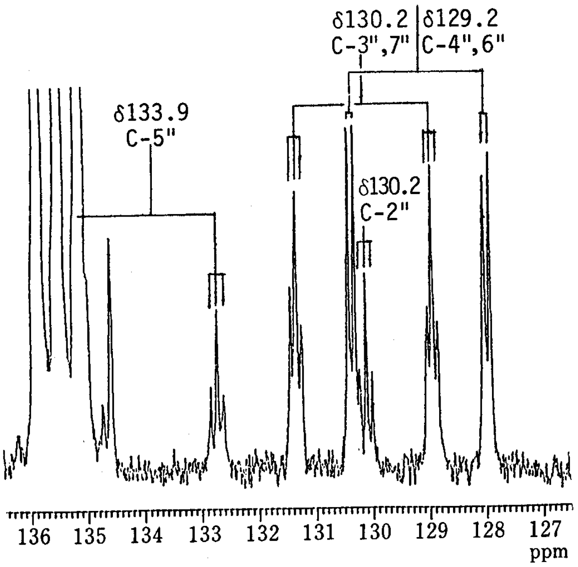

Fig. 2. Nondecoupled Spectra

at C-12.

From the complete-decoupled (COM) and off-resonance (OFR) spectra, the signals at δ 130.2 and 133.9 each appeared to be due to one carbon, and those at δ 129.2 and 130.2 each appeared to be due to two carbons. Examination of the nondecoupled spectrum (Fig. 2) allowed assignment of the aromatic carbons (Table I). The carbon–proton coupling constants were as follows: ${}^{1}J_{C_3H_3}=162$ Hz, ${}^{3}J_{C_3H_5}=6.8$ Hz. The assignments of two tertiary carbons at

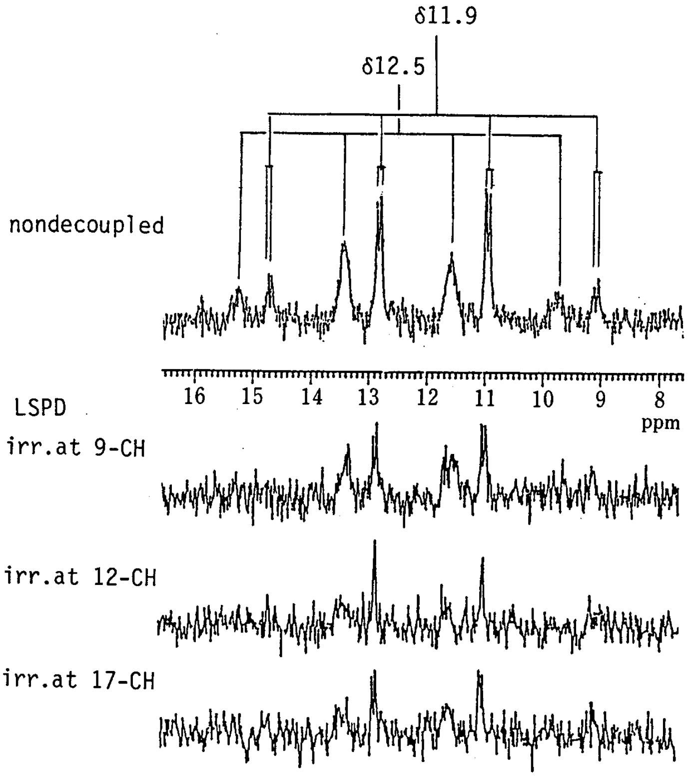

Fig. 3. Nondecoupled and LSPD Spectra

C-18 and C-19 were hitherto made by reference to the calculation based on additive shift parameters. An application of the LSPD technique enabled them to be determined definitely. Irradiation of the proton signal at δ 1.53 (9-CH) increased the intensity of the carbon signal at δ 12.5, and irradiation of the signal at δ 5.38 (12-CH) eliminated the splitting of the signal at δ 11.9 (Fig. 3). Therefore, the carbon signal at δ 12.5 was assigned to C-19 and that at δ 11.9 to C-18.

Experimental

NMR spectra were run on a JEOL GX-270 (^{1}H-NMR at 270.05 MHz, ^{13}C-NMR at 67.80 MHz) spectrometer in C_5D_5N with tetramethylsilane as an internal standard.

Cynafogenin (1)——^{1}H-NMR δ: 1.03 (3H, s, 18-Me), 1.42 (3H, s, 19-Me), 1.53 (1H, t, $J=10$ Hz, 9-CH), 1.75 (3H, s, 2′-Me), 2.05 (3H, s, 21-Me), 3.22 (1H, dd, $J=8.6$, 5.0 Hz, 17-CH), 3.85 (1H, tt, $J=11$, 5.0 Hz, 3-CH), 5.38 (1H, d, $J=10$ Hz, 12-CH), 5.72 (1H, t, $J=10$ Hz, 11-CH), 7.49 (2H, dt, $J=7.3$, 1.5 Hz, 4″, 6″-CH), 7.57 (1H, tt, $J=7.3$, 1.5 Hz, 5″-CH), 8.33 (2H, dt, $J=7.3$, 1.5 Hz, 3″, 7″-CH). ^{13}C-NMR see Table I.

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