Note

Carbon-13 NMR Spectra of Cotylenins

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In previous papers structural elucidation of cotylenins,¹⁾ new plant growth regulators isolated from an unidentified species of *Cladosporium*, was reported on the basis of chemical and spectroscopic evidence; the presence of both acetal and ketal carbons in the complex molecule cotylenin A was shown by carbon-13 NMR spectrometry. In addition, we have isolated a new cotylenin (cotylenin I: mp 91~4°C, C₃₃H₅₄O₈) and assigned the structure V (4'-O-(1,1-dimethylallyl)-cotylenin E) to this minor metabolite.²⁾ Recently, the assignments of the carbon-13 NMR spectra of fusicoccin and its derivatives, and a new fusicoccin³⁾ having an additional hydroxyl function at C₃ were achieved by L. Radics *et al.*⁴⁾ In this paper we wish to report the carbon-13 NMR(CMR) spectra of cotylenins which reasonably interpret their proposed structures: signal assignments of the aglycone carbons were principally made by comparison with those of the new fusicoccin closely related to cotylenins and those of the sugar moiety carbons in cotylenin A by the observed acetylation shifts and selective decoupling experiments.

CMR spectra of cotylenol (I, the common aglycone of cotylenins), cotylenin A (II) and its derivatives were recorded in *d*-chloroform and those of the others (cotylenins C(III), E(IV), F(V) and I(VI)) in *d*⁴-methanol (Table I). Chemical shifts of the new fusicoccin (VII) in *d*⁶-dimethylsulfoxide-*d*-chloroform (1:2) are cited in

Table I.⁴⁾ The CMR spectra of I and II provided the assignments of C₉ (the site of glycosylation) and C₁₀.⁵⁾ As expected, the majority of signal shifts due to the aglycone carbons of IV (the shift values in *d*⁶-dimethylsulfoxide-*d*-chloroform) were in good agreement with those of VII; the signal assignments of C₈, C₇, C₈(C₉), C₁₅, C₁₇ and C₁₈ were also supported by selective decoupling experiments on II (C₈-H: δ ca. 3.15, C₇-H: δ ca. 2.0, C₈ and C₉-H: δ ca. 3.9, C₁₀-H: δ ca. 3.35, C₁₇-H: δ 0.79 and C₁₈-H: δ 1.27), and the signals of the vicinally located C₄ and C₆ were observed as rather broadened triplets in the off-resonance spectra.⁶⁾ However, the signal shifts of the carbons C₁, C₂, C₁₂, C₁₃, C₁₄ and C₁₆ in IV and VII were considerably different. The differences except that of C₂ are reasonably interpreted on the basis of the hydroxylation shifts (α -, β - and γ -effect)⁸⁾ in VII. The up-field shift of C₂ in VII can be explained by a comparable effect of *endo*-5-hydroxyl group on C₂ (+2.8 ppm) in *endo*-5-hydroxynorbornene⁷⁾ (the proximity of the hydroxyl function at C₁₂ to the C_{1,2}-double bond was shown by the formation of a cyclic ether linkage between C₁₂ and C₂).⁹⁾

Then, the signals due to the sugar moiety carbons in II were readily assigned by the chemical shifts and signal multiplicities. The signal assignments of C_{1'}, C_{2'}, C_{3'} and C_{2''} were supported by selective decoupling experiments on II (C_{1'}-H: δ 5.08, C_{2'}-H: δ 3.59, and C_{3'}-H: δ 4.03) and the acetylation shifts in a lithium aluminum hydride reduction product of II (C_{2',3''}-diacetate; C_{1'}: -1.2, C_{2'}: +1.2, C_{3'}: -2.9, C_{2'}: -0.7 and C_{3''}: +3.2 ppm). Signals due to the sugar moiety carbons in III, IV, V and VI were tentatively assigned as shown in Table I.^{5,9)} The difference in chemical shifts of C_{2''} in II and III is similar to that in furanoses and pyranoses.¹⁰⁾ Appearances of C_{4'}- and C_{6''}-signal in III at a higher field in comparison with those in II (C_{5''}) and V (C_{4'}) can be interpreted by 1,3-diaxial interaction between C_{4'}-H and C_{2''}-C_{6''}.^{1,11)} As expected, the CMR spectrum of V was closely similar to that of VI except signals due to the sidechain carbons in the sugar part. The presence of a 1,1-dimethylallyl group at C_{4'} in V is clearly indicated by comparison of the CMR spectra of V, VI and VII.

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TABLE I. CARBON-13 CHEMICAL SHIFTS (δ ppm from TMS)

Carbon No.	I	II	III	IV	V	VI	VII
1	133.9	134.8	135.5	135.6 (133.4) ^b	135.6	135.3	127.6
2	139.2	139.3	141.1	141.2 (140.0)	141.5	141.4	144.6
3	81.7	82.0	83.4	83.2 (81.5)	83.4	83.2	82.2
4	31.4	31.7	32.7	32.3 (31.4)	32.7	32.5	31.7
5	35.1	35.3	35.8	35.5 (34.7)	35.9	35.7	35.2
6	40.0	40.4	41.7	41.4 (40.0)	41.7	41.6	40.7
7	41.7	41.4	42.7	42.5 (41.2)	42.8	42.6	41.6
8	77.3	78.0 Δ	79.0 Δ	79.0 (77.0) Δ	79.1 Δ	78.7 Δ	77.8
9	67.4	78.4 Δ	79.8 Δ	79.6 (77.8) Δ	79.7 Δ	79.5 Δ	78.1
10	136.5	134.8	136.7	137.8 (135.5)	137.0	136.5	135.0
11	51.7	51.9	53.2	53.1 (51.6)	53.2	53.0	52.4
12	42.2	42.4	43.8	43.3 (42.2)	43.7	43.6	82.0
13	26.7	26.9	27.6	27.0 (27.5)	27.5	27.4	34.7
14	149.1	149.9	150.6	150.2 (147.9)	150.8	150.5	144.1
15	27.5	28.2	29.3	28.5 (26.4)	29.1	29.1	27.6
16	77.3	77.3	78.1	78.5 (77.0)	78.2	77.3	76.9
17	8.2	8.4	9.1	8.7 (8.3)	9.0	9.0	8.5
18	26.0	25.6	26.6	26.1 (25.9)	26.8	26.7	23.4
19	21.0°	21.5°	22.1°	21.5 (21.3)°	21.9°	21.9°	21.1°
20	19.8°	20.6°	21.2°	20.6 (20.5)°	21.1°	21.1°	20.4°
1'		101.6	103.6	103.5 (102.0)	103.4	103.2	102.2
2'		72.7	71.2	73.4°(72.0)	72.5	72.7	72.1
3'		81.4	77.9	75.2 (73.4)	73.7	73.6	73.6
4'		106.1	70.8	71.7 (69.9)	75.4	74.9	70.9
5'		66.4	68.1	72.7 (71.0)	72.5	72.7	71.5
6'		70.1	72.0	73.4°(71.6)	71.7	72.1	62.8
1''		104.0	97.2		67.9	27.6×	25.8×
2''		85.2	75.4		78.2	78.0	75.0
3''		52.7	57.1		57.3	146.4	144.1
4''		44.1	44.1		44.5	112.8	113.5
5''		18.4	13.3		16.6	27.9×	25.9×
OMe	59.1	59.3	59.8	59.6 (58.8)	59.6	59.5	59.1
		59.3	59.7	59.6 (58.8)	59.3	59.1	

^a Broad signal.Spectra taken with a Hitachi R-26 (10.0 MHz, I and IV (*d*⁴-methanol)), a Bruker HFX-90 (22.63 MHz, II) and a JEOL JNM-FX-100 (25.15 MHz, III, IV (*d*⁶-dimethylsulfoxide-*d*-chloroform), V and VI) NMR spectrometer at ambient probe temperature (25~30°C).^b *d*⁶-Dimethylsulfoxide-*d*-chloroform (1:2). Δ , ° and ×; assignments may be reversed in each vertical column.

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