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CYPERENYL ACETATE AND CYPERENAL FROM *CIRSIUM DIPSACOLEPIS*

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Key Word Index—*Cirsium dipsacolepis*, Compositae; cyperene, cyperenyl acetate, cyperenol, cyperenal; cyperenic acid, ^{1}H NMR, ^{13}C NMR

Abstract—Two new sesquiterpenes, cyperenyl acetate and cyperenal have been isolated from *Cirsium dipsacolepis*. ^{13}C NMR assignments of cyperene derivatives have been also investigated

INTRODUCTION

In the course of our studies on the constituents of the root of *Cirsium dipsacolepis* (Maxim) Matsum., we have isolated two new and six known aliphatic aldehydes as minor components, and have already reported the structures of these compounds [1], 7-octenal, (2*E*)-2,8-nonadienal, (2*E*)-2,9-decadienal, (2*E*)-2,10-undecadienal, (2*E*,4*E*)-2,4,10-undecatrienal, and (2*E*,4*E*)-, (2*Z*,4*Z*)- and (2*E*,4*Z*)-2,4,11-dodecatrienal. The present investigation of the constituents of *C dipsacolepis* resulted in the isolation of two cyperene derivatives, cyperenyl acetate (**3**) and cyperenal (**4**) Teisseire *et al* [2] synthesized cyperenyl acetate and cyperenal from cyperene (**1**) in their study on the structure of norpatchoulenol. However, no physical properties of these compounds were reported This paper deals with ^{13}C NMR assignments of cyperene derivatives

RESULTS AND DISCUSSION

The IR and NMR spectra suggested that compound **3** had an acetate group In the ^{1}H NMR spectrum, the signals of three methyl groups were observed at δ0.76 (3H, *s*), 0.80 (3H, *d*, $J = 6$ Hz) and 0.94 (3H, *s*), which were similar to those of cyperene (**1**) [1] except for the absence of a singlet at δ1.62 (3H) Furthermore, ^{13}C NMR spectra of compounds **1** and **3** agreed well except for the signals of C-3, C-4 and C-5, whose chemical shift differences were 1.3–6.7 ppm as shown in Table 1 Disappearance of the methyl carbon signal (C-14) of cyperene at δ14.2 and appearance of the methylene carbon signal (C-14) of compound **3** at δ62.0 indicated that compound **3** was cyperenyl acetate Moreover, hydrolysis of **3** with 3 N NaOH–MeOH (1:10) at room temp. for 1 hr afforded cyperenol (**2**) [3]. Based on these results, the structure of compound **3** is established to be cyperenyl acetate,

Table 1. ^{13}C NMR spectra of cyperene derivaties

Carbon	Cyperene	Cyperenol	Δ*	Cyperenyl acetate	Δ*	Cyperenal	Δ*	Cyperenic acid	Δ*
	Chemical shifts (δ, ppm)								
1	65.7	66.0	0.3	66.1	0.4	68.7	3.0	68.4	2.7
2	26.3	26.1	−0.2	26.0	−0.3	25.6	−0.7	25.9	−0.4
3	42.3	37.9	−4.4	38.2	−4.1	33.9	−8.4	36.6	−5.7
4	127.7	131.2	3.5	126.4	−1.3	134.5	6.8	122.9	−4.8
5	142.2	146.3	4.1	148.9	6.7	176.6	34.4	169.3	27.1
6	27.6	27.6	0	27.6	0	28.3	0.7	31.5	3.9
7	48.7	48.6	−0.1	48.5	−0.2	48.2	−0.5	48.3	0.4
8	27.8	27.6	−0.2	27.6	−0.2	27.1	−0.7	27.1	−0.7
9	28.3	28.1	−0.2	28.1	−0.2	27.9	−0.4	28.0	−0.3
10	35.3	35.3	0	35.4	0.1	36.1	0.8	36.1	0.8
11	41.4	41.2	−0.2	41.2	−0.2	41.6	0.2	41.9	0.5
12	26.1	26.1	0	26.0	−0.1	26.2	0.1	26.4	0.3
13	19.4	19.3	−0.1	19.3	−0.1	19.3	−0.1	19.4	0
14	14.2	60.7	46.5	62.0	47.8	188.2	174.0	173.2	159.0
15	18.0	17.9	−0.1	17.9	−0.1	18.0	0	18.1	0.1
16				171.0					
17				21.0					

*Δ. Chemical shift difference from cyperene

which has been found for the first time as a natural product.

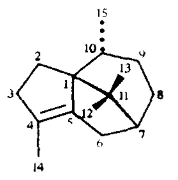
Furthermore, cyperene isolated from *C. dipsacolepis* was reacted with selenium dioxide (one equivalent mol) in acetic anhydride–acetic acid (59:1) for five days at 60°C under nitrogen atmosphere to afford cyperenyl acetate in 54% yield, which was identical with natural cyperenyl acetate.

In the ^1H NMR spectrum of compound **4**, three signals assigned to methyl groups were also observed at δ0.82 (3H, *s*), 0.84 (3H, *d*, $J = 6$ Hz) and 1.02 (3H, *s*), which was similar to those of cyperene and cyperenyl acetate **3**. Furthermore, a singlet (1H) at δ9.84 and an IR absorption band at 1670 cm^{-1} suggested the presence of a conjugated aldehyde group in compound **4**. Based on these results and other spectral data compound **4** was deduced to be cyperenal. When cyperenol (**2**) was treated with pyridinium dichromate in methylenechloride under nitrogen atmosphere at room temperature for eight hr, it afforded cyperenal (**4**). These results clearly indicate that compound **4** is cyperenal, which has also been found for the first time as a natural product.

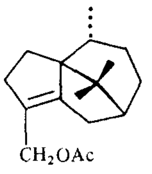
^{13}C *NMR of cyperene derivatives*

Joseph-Nathan *et al.* [4] had studied the ^1H and ^{13}C NMR spectra of cyperene using 2D techniques. Based on their assignments of the ^{13}C NMR spectrum of cyperene, those of cyperenyl acetate could be readily made, since only small chemical shift changes were observed at C-3, C-4 and C-5 as shown in Table 1. In order to confirm these assignments, the ^{13}C NMR spectrum of cyperenol was measured, which supported the assignments of cyperenyl acetate. These were also confirmed by INEPT experiments.

On the other hand remarkable chemical shift changes



1



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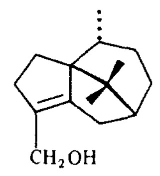

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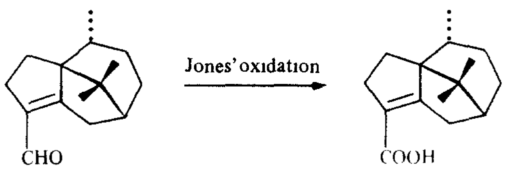

4 **5**

were observed in the ^{13}C NMR spectrum of cyperenal as shown in Table 1 However, tentative assignments could be made by INEPT experiments and by comparing the chemical shifts with those of cyperenic acid (**5**), obtained from cyperenal by Jones' oxidation [3] There was no problem in the assignments of cyperenic acid. However, the assignments of C-2, C-3, C-6 and C-8 of cyperenal were interchangeable Therefore, the C-2, C-3, C-6 and C-8 carbons were finally assigned by using ^{1}H–^{1}H homonuclear and ^{1}H–^{13}C heteronuclear chemical shift correlation spectra Thus, the assignments of cyperene derivatives were established as shown in Table 1

EXPERIMENTAL

Extraction and isolation Procedures were similar to those described in the preceding paper [1]

Cyperenyl acetate (**3**) Oil, $[\alpha]_D$ −5.1° (CHCl$_3$, *c* 0.8), ^{1}H NMR (270 MHz, CDCl$_3$) δ0.76 (3H, *s*, H-12), 0.80 (3H, *d*, *J* = 6 Hz, H-15), 0.94 (3H, *s*, H-13), 2.02 (3H, *s*, H-17), 4.59 (2H, AB*q*, *J* = 12.8 Hz, H-14), ^{13}C NMR, Table 1, IR ν_{max}^{film} cm^{-1} 1725, 1240, 1020 and 960, EIMS *m/z* 262 (M^+ $C_{17}H_{26}O_2$)

Cyperenal (**4**) Oil, $[\alpha]_D$ 9.6° (CHCl$_3$, *c* 0.4), ^{1}H NMR (CDCl$_3$) δ0.82 (3H, *s*, H-12), 0.84 (3H, *d*, *J* = 6 Hz, H-15), 1.02 (3H, *s*, H-13), 9.84 (1H, *s*, H-14), ^{13}C NMR, Table 1, IR ν_{max}^{film} cm^{-1} 1670, EIMS *m/z* 218 (M^+ $C_{15}H_{22}O$)

Cyperenic acid (**5**) Obtained from cyperenal by Jones' oxidation Oil, $[\alpha]_D$ −13.7° (CHCl$_3$, *c* 0.3), ^{1}H NMR (CDCl$_3$) δ0.83 (3H, *s*, H-12), 0.86 (3H, *d*, *J* = 6 Hz, H-15), 1.00 (3H, *s*, H-13), ^{13}C NMR, Table 1, IR ν_{max}^{film} cm^{-1} 1700, EIMS *m/z* 234 (M^+ $C_{15}H_{22}O_2$)

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KANSHONES A AND B, SESQUITERPENOIDS OF *NARDOSTACHYS CHINENSIS*[*]

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Key Word Index—*Nardostachys chinensis*, Valerianaceae, sesquiterpenoid, kanshones A and B

Abstract—Two new sesquiterpenoids, kanshones A and B, isolated from *Nardostachys chinensis* were fully characterized by chemical and spectroscopic means.

INTRODUCTION

Nardostachys chinensis Batalin (Japanese name: Kanshōkō), a valerianaceous plant, the roots and rhizomes of which have been used in Oriental medicine is a rich source of sesquiterpenoids [1–9]. As a continuation of our earlier work [10], we have now isolated two new sesquiterpenoids, kanshones A and B, in addition to the major constituent nardosinone (**3**), from the methylene chloride extract of this plant material The structures of these sesquiterpenoids were established on the basis of detailed spectral analysis and chemical transformations to compounds of known structure

RESULTS AND DISCUSSION

Kanshone A isolated as oil, $[\alpha]_D$ −147.8°, was analysed for $C_{15}H_{22}O_2$ on the basis of its mass ion peak at *m/z* 234 [M^+] and from its ^{13}C NMR spectrum which showed resonances for 15 carbon atoms. The UV absorption maximum at 248 nm and IR spectral bands at 3450 and 1665 cm^{-1} indicated that kanshone A bears a hydroxyl group and a conjugated carbonyl function. The ^{1}H NMR spectrum of kanshone A showed a signal assigned to a β-hydrogen of an enone system at δ 7.00 (1H, *d*, *J* = 4.0 Hz) as well as those due to three hydrogens of an ABX system at 2.62 (1H, *dd*, *J* = 7.1 and 1.0 Hz), 6.16 (1H, *dd*, *J* = 10.0 and 1.0 Hz) and 6.96 (1H, *dd*, *J* = 10.0 and 7.1 Hz) These data, along with the ^{13}C NMR signals at δ 128.9 (*d*), 137.2 (*d*), 141.6 (*s*), 151.1 (*d*) and 187.9 (*s*), revealed that the carbonyl group was flanked by two double bonds In addition to above, the ^{1}H NMR spect-

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[*] 'Sesquiterpenoids', Part 61 Also Part 126 in the series, 'The Validity of the Oriental Medicines'

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