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ALKALOIDS OF ACONITUM COREANUM

VI. STRUCTURE OF ACORIDINE

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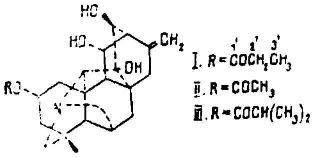
UDC 547.944/945

The new C_{20}-diterpene alkaloid acoridine has been isolated from the epigeal part of *Aconitum coreanum* (Levl.) Rapaics, and the structure of 14-hydroxy-2-propionylhetisine has been established for it on the basis of spectral characteristics. Acoridine is the first diterpene alkaloid esterified by propionic acid.

Continuing a study of the alkaloid composition of the plant *Aconitum coreanum* (Levl.) Rapaics, we have investigated the epigeal part of the plant collected in the withering phase in the environs of the village of Chernyatino, Maritime Territory. The concentration of alkaloids amounted to 1.05% on the weight of the air-dry raw material. From the total alkaloids we isolated by chromatography 13-acetyl-14-hydroxy-2-isobutyrylhetisine [1] and its N-oxide [2], 14-hydroxy-2-isobutyrylhetisine [3] and its N-oxide [4], and 2-acetyl-14-hydroxyhetisine (acorine) [3], and also an optically active base with mp 204-206°C (I). Base (I) had the composition $C_{23}H_{31}NO_5$ (HRMS).* Its IR spectrum showed absorption bands at 3370 cm^{-1} (OH) and 1730 cm^{-1} (C=O). In its PMR spectrum, signals appeared the chemical shifts and multiplicities of which almost coincided with those of acorine (II) and of 14-hydroxy-2-isobutyrylhetisine (III), with the only difference that the spectrum of (I) contained a quartet at 2.28 ppm (2 H, J = 7.5 Hz) and a triplet at 1.07 ppm (3 H, J = 7.5 Hz) in place of the signals of the protons of an acetoxy group in the spectrum of (II) (δ 1.99 ppm, 3 H) and the signals of the protons of an isobutyryloxy group in the spectrum of (III) (δ 2.45 ppm, 1 H and 1.12 ppm, 6 H). These facts showed that (I) was 14-hydroxy-2-propionylhetisine. We have called the new base acoridine.



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*The high-resolution mass spectrum was taken by Yu. M. Mil'grom.

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 91-93, January-February, 1991. Original article submitted April 28, 1990.

TABLE 1. Chemical Shifts of the Carbon Atoms of Acoridine (I), Acorine (II), and 14-Hydroxy-2-isobutyrylhetisine (III) in $CDCl_3$ (δ, ppm)

C atom	Multiplicity	I	II [3, 6]	III [3, 5, 6]
1	t	31,15	31,22	31,37
2	d	69,92	70,06	69 69
3	t	36,76	36,57	36,82
4	s	37,65	37,49	37.65
5	d	69,06	69,13	69,05
6	d	63,12	63,12	63 11
7	t	32,05	32,04	32,04
8	s	44,37	44.17	44,37
9	d	53,63	53,63	53,63
10	s	46,46	46,37	46,39
11	d	76,04	76,19	76,04
12	d	52,66	52,76	52,81
13	d	79,85	79,99	79,92
14	s	80,37	80,27	80,37
15	t	31,15	31,22	31,15
16	s	144,91	144,76	144,60
17	t	108,16	108,23	108,16
18	q	29,73	29,73	29,73
19	t	63,12	63,12	63,11
20	d	69,24	69,24	69,24
1'C=O	s	174,01	171,20	176,69
2'		28,31 (t)	21,59 (q)	34,51 (d)
3'	q	9,19	—	19,12

The structure (I) proposed for acoridine was confirmed completely by its ^{13}C NMR spectrum. The assignment of the CSs of the signals of the carbon atoms (Table 1) was carried out on the basis of their multiplicities in the spectrum of (I) obtained under the conditions of incomplete suppression of coupling with protons, and by comparison with the CSs of the spectra of (II) and (III) [3, 5, 6]. A comparative analysis of the ^{13}C NMR spectra of (I-III) showed that the signals of the carbon atoms of the C_{20}-diterpene skeleton practically coincided. As was to be expected, their difference consisted only in the fact that in the spectrum of (I) there were signals in the form of a triplet at 28.31 ppm and a quartet at 9.19 ppm from the carbon atoms of the propionyl substituent in place of the signal from the methyl group at 21.59 ppm in the spectrum of (II) and the signals from the isobutyryl group at 34.51 and 19.12 ppm in the spectrum of (III).

The mass spectrum of acoridine contained strong peaks of ions with m/z 401 (M^+), 384 $(M-17)^+$, 373 $(M-28)^+$, 356 $(M-45)^+$, 345 $(M-56)^+$, 328 $(M-73)^+$. These facts indicated that the fragmentation of acoridine under mass-spectrometric conditions was similar to that of (II) and (III) [3, 6], with the exception of the formation of the ion with m/z 328. The latter was formed as the result of the ejection from the molecular ion of (I) of a prionyloxy group in place of the acetoxy and butyryloxy groups in (II) and (III), respectively. Thus, acoridine is the first diterpene alkaloid esterified with propionic acid.

EXPERIMENTAL

IR, mass, ^1H, and ^{13}C NMR spectra were obtained on UR-20 (KBr), MKh-1310 and MS-3301, and BS-567 A, 100 and 25.142 MHz, instruments (δ scale, $CDCl_3$, 0 – HMDS for the PMR spectra and 0 – TMS for the ^{13}C NMR spectra).

Chromatographic monitoring was carried out by TLC (LSL 5/40 alumina, neutral) in the solvent systems chloroform–methanol (25:1) and (20:1).

Isolation of the Alkaloids. The air-dry comminuted epigeal part of the plant (7400 g) was extracted with chloroform by the method described in [3]. When the acid solution was made alkaline with sodium carbonate (pH 8) and the alkaloids were then extracted with chloroform, a total of 64 g of alkaloids was obtained. The solution was then made alkaline with caustic soda (pH 12), and extraction with chloroform gave 14 g of strongly basic alkaloids.

The mixture of alkaloids (64 g) was chromatographed on alumina (Brockman, activity grade II, neutral, deactivated, 1:100). The first hexane–ether eluates gave a mixture of nonpolar fractions; from them by rechromatography of the fractions on alumina and silica gel were isolated 13-acetyl-14-hydroxy-2-isobutyrylhetisine, mp 181-182°C (from acetone)

(0.12 g) and its N-oxide, mp 242-244°C (from acetone) (0.01 g). In a similar manner, the ethereal eluates yielded 14-hydroxy-2-isobutyrylhetisine, mp 230-231°C (from acetone) (0.95 g) and its N-oxide, mp 316-319°C (from ethanol) (0.43 g). The chloroform fractions gave a crystalline mixture of alkaloids containing mainly acorine (6.08 g). Chromatography of the mother liquors led to the isolation of acoridine (0.057 g) and acorine (0.82 g).

Acoridine, mp 204-206°C, $[\alpha]_D$ +16° (c 0.663; methanol) had the form of colorless needles from acetone and chloroform. It was readily soluble in chloroform, methanol, and ethanol.

Mass spectrum, m/z (%): 401(M^+, 100), 384(72), 373(72), 356(86), 345(54), 328(75), 312(43), 310(18), 300(18), 300(18), 272(14), 146(21), 105(21), 94(14), 91(20), 79(12).

PMR spectrum, δ (ppm): 5.08 (1H, br.s., H-2), 4.99 and 4.60 (br.s, 1H each, $=CH_2$), 4.15 (1H, d, J = 9 Hz, H-11), 3.98 (1H, br.s, H-13), 3.46 (1H, s, H-20), 3.05 (1H, br.s, H-6), 2.91 and 2.48 (d, 1H each, J = 12 Hz, H_α-19 and H_β-19, respectively), 2.84 (1H, d, J = 16 Hz, H_α-1), 2.42 (1H, br.s, H-12), 2.28 (2H, q, J = 7.5 Hz, $C\underline{H_2}-CH_3$), 2.00-1.90 (3H, sharp signal, H-9, H_α, H_β-15), 1.90-1.70 (3H, m, H_β-1, H_α-3, H-7), 1.64 (1H, dd, J = 15.5 and 4 Hz, H_β-3), 1.48 (1H, s, H-5), 1.33 (1H, J = 14 and 3 Hz, H-7), 1.07 (3H, t, J = 7.5 Hz, $CH_2-C\underline{H_3}$), 0.86 (3H, s, CH_3-18).

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