^{13}C NMR spectra of a correlation with isonitramine, and also by direct comparison with a synthesized sample.

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ALKALOIDS OF *Aconitum coreanum*. I. STRUCTURE OF ACORINE

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Two C_{20}-diterpene alkaloids have been isolated from the epigeal part of *Aconitum coreanum* (Levl.) Rapaics: the known 14-hydroxy-2-isobutyrylhetesine (I) (Guan-Fu base Z) and a new one — acorine (II), $C_{22}H_{29}NO_5$, mp 214-215°C (from acetone), α_D^{20} + 9° (c 0.01; methanol), for which the structure of 2-acetyl-14-hydroxyhetesine has been established. Details of the IR, mass, and ^{13}C NMR spectrum of (I) and (II) and of the PMR spectrum of (II) are given.

Korean monkswood (*Aconitum coreanum* (Levl.) Rapaics (A. Komarovii Steinb.) is occasionally found in low oak woods and thickets of Siberian filbert of the southern part of the Maritime Territory [1, 2], in north-eastern China, and on the Korean peninsula. A crystalline hydrobromide of a base with the composition $C_{35}H_{41}NO_{10}$ has been isolated previously from the epigeal part of this plant [3]. The presence of hypoconitine and a number of new alkaloids that are acyl derivatives of 14-hydroxyhetesine in it has been established [4].

We have investigated the epigeal part of the plant collected in the environs of the village of Chernyatino, Maritime Territory, in the flowering period. The amount of combined alkaloids was 0.8% on the weight of the air-dry raw material. By chromatography, from the mixture of alkaloids we obtained two individual crystalline bases with mp 229-230°C (I) and 214-215°C (II). Base (I) had the composition $C_{24}H_{33}NO_5$ (M^+ 415.2358 (HRMS)). Its IR spectrum contained absorption bands of hydroxy and carbonyl groups (3400 and 1745 cm^{-1}). Its PMR spectrum showed signals the chemical shifts and multiplicities of which agreed completely with those published for Guan-Fu base Z, mp 230-231°C, isolated from Korean monkswood growing in China [5]. For the latter the structure of 14-hydroxy-2-isobutyrylhetesine has been established on the basis of the results of an analysis of its 1-D and 2-D NMR spectra. The strongest peaks in the mass spectrum of (I) were the following (m/z, %): 415(82), 398(88), 387(89), 370(100), and 328(70). The results obtained indicate that the base obtained was identical with the Guan-Fu base Z.

Base (II), with the composition $C_{22}H_{29}NO_5$ (M^+ 387.2038 (HRMS)) was not optically active; it had the same absorption bands in the IR spectrum as (I): 3400 cm^{-1} (OH) and 1745 cm^{-1} (C=O). A comparison of the PMR spectra of (I) and (II) showed that they were close, differing by the fact that in the spectrum of (II), in place of the signals of the isobutyryl substituent (δ 2.47 and 1.12 ppm), there was a singlet from the protons of an acetoxy group at 1.99 ppm.

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TABLE 1. Chemical Shifts of the Carbon Atoms of Base Z and of Acorine in $CDCl_3$ (δ, ppm)

C-atom	Guan-Fu base Z	Acorine	C-atom	Guan-Fu base Z	Acorine
1	31,37	31,22	13	79,95	79,99
2	69,56	70,06	14	80,23	80,27
3	36,71	36,57	15	31,06	31,22
4	37,61	37,49	16	144,65	144,76
5	59,93	60,13	17	108,17	108,23
6	63,03	63,12	18	29,70	29,73
7	31,96	32,04	19	62,98	63,12
8	44,30	44,17	20	69,12	69,24
9	53,51	53,63	1′	176,51	171,20*
10	46,33	46,37	2′	34,41	21,59
11	76,04	76,19	3′	19,98	
12	52,66	52,73			

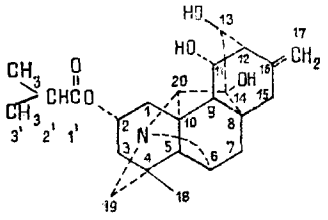
*The chemical shift was measured at an increased concentration with the addition of a methanolic solution of acorine.

This gave grounds for considering that (II) was 2-acetyl-14-hydroxyhetesine. We have called the new base acorine.

The structure (II) suggested for acorine was confirmed completely by an analysis of its ^{13}C NMR spectrum.

The signals were identified by comparing the spectrum of (II) taken under the conditions of complete and incomplete decoupling from protons with the spectrum of base Z, illustrations and the parameters of the ^1H and ^{13}C NMR spectra of which have been given in [5]. The assignment of the signals was made by a 2-D NMR heteronuclear correlation experiment.

A comparison of the spectra (Table 1) showed that the spectrum of acorine contained a quartet at 21.59 ppm, characteristic for an acetoxy group, in place of the signals from the carbon atoms 3' and 2' of the isobutyryl substituent present in the spectrum of base Z. The most pronounced changes were observed for the signals of carbon atoms 1' and 2'. The remaining signals has close values of their chemical shifts (deviations in the range of 0.03-0.0.19 ppm).



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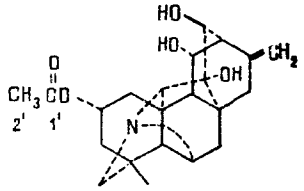

II

It followed from the mass spectrum of acorine — m/z, %: 387(95), 370(100), 359(87), 342 (97), 328(64) — that its breakdown under the conditions of mass spectrometry was analogous to that of (I) with the only difference that the ion with m/z 328 was formed as the result of the ejection from the molecular ion not of a butyryloxy but of an acetoxy group. A measurement of the elementary compositions of the M −17, M −28, and M −45 ions in (I) and (II) showed that they were obtained by the splitting out of OH, CO, and CO_2H groups, respectively.

The saponification of acorine under the conditions of alkaline hydrolysis formed an amino alcohol with the composition $C_{20}H_{27}NO_4$ (III), the IR spectrum of which lacked the absorption band of a carbonyl group.

The results obtained confirmed the structure (II) suggested for acorine.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer from the substances in the form of tablets with KBr, mass spectra on MKh-1310 and MS-3301 instruments, NMR spectra on a BS-567A, 100 MHz spectrometer (δ scale, $CDCl_3$, 0 — HMDS for the PMR spectrum; 0 — TMS for the ^{13}C NMR spectrum).

Chromatographic monitoring was performed by TLC (LSL 5/40 alumina, neutral; in the chloroform—methanol (20:1, 10:1, 4:1) solvent systems.

Isolation of the Alkaloids. The air-dry comminuted epigeal part of the plant (1950 g) was wetted with a 5% solution of sodium carbonate, and the alkaloids were extracted with chloroform. The chloroform extract was shaken with a 5% solution of sulfuric acid. With cooling, the acid solution was made alkaline with sodium carbonate, and the alkaloids were exhaustively extracted with chloroform (14 g). The aqueous solution was made alkaline with caustic soda and reextracted with chloroform (2 g). The combined alkaloids (14 g) were chromatographed on alumina (Al_2O_3 with Brockmann activity grade II, neutral, deactivated, 1:100). Hexane–ether eluates yielded 70 mg of (I) and 250 mg of (II).

Guan-Fu-base Z (I), mp 229-230°C. It crystallized from hexane–ether and acetone in the form of colorless needles readily soluble in chloroform.

Acorine (II) mp 214-215°C, $[\alpha]_D^{20}$ +9 (c 1.01; methanol). It crystallized in the form of colorless needles from acetone. It was readily soluble in methanol and less readily in chloroform.

PMR spectrum, δ, (ppm): 5.08 (1H, m, H-2), 483 and 464)(br. s,1H) each = CH_2), 4.18 (1H and J = 9 Hz, H-11), 4.00 (1H, br. s, H-13), 3.48 (1H, s, H-20), 3.06 (1H, br. s, H-6), 2.92 and 2.48 (d, 1H each, J = 12 Hz, H_α-19, H_β-19, respectively, 2.86 (1H, J=16 Hz, H_α = 1, 2.40-2.60 (1H, m, H-12), 2.60-1.64 (6H, m, H_α,H_β=15, H-9, H_β-1, H-7, H_α-3), 1.99 (3H, s, $OcOCH_3$), 1.53 (1H, dd, J - 15.5 and 4.5 Hz, H_β-3), 1.48 (1H, s, H-5), 1.32 (1H, dd, J = 13.9 and 2.4 Hz, H-7), 0.96 (3H, s, CH_3-18).

Hydrolysis of Acorine. A solution of acorine (30 mg) in 5% methanolic KOH solution was boiled in the water bath for 1 h. After the elimination of the solvent, the residue was treated with water and was shaken with chloroform. The chloroform extract was dried, filtered and evaporated. The residue was amorphous substance. Mass spectrum, m/z (%): 345 (M^+, 100), 328 (M −17,88), 317 (M −28,87), 300 (M −45,86).

CONCLUSIONS

From the epigeal part of *Aconitrum coreanum* (Levl. Rapaics), in addition to the known alkaloid 14-hydroxy-2-isobutyrylhetesine (Guan-Fu base Z), the new alkaloid acorine has been isolated, and its structure has been established as 2-acetyl-14-hydroxyhetesine.

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