

SESQUITERPENE ALCOHOLS FROM *HEDYCHIUM SPICATUM*  
VAR. *ACUMINATUM*

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*Hedychium spicatum* Hem. var. *acuminatum* (Zingiberaceae), commonly known as "Kapurkachri," is a perennial herb that grows wild in parts of the central Himalayas at elevations of 3000-8000 ft. Its rhizomes have a strong aromatic odor and are reputed to be of value in medicine and perfumery (1). They are used in the treatment of stomach ailments, pain, and inflammation (2), and the ethanolic extract of the rhizomes has been reported to possess anti-inflammatory activity (3,4). In addition, the essential oil from the whole plant has been reported to be lethal to larvae of the beetle *Dermestes frischii* (5).

Earlier reports (6-8) on the chemical composition of the essential oil from rhizomes of *H. spicatum* are in agreement on the presence of 1,8-cineole (27.1-56.2%) and linalool (6.8-18.0%) as major components, but they do not explain the claimed high ester values of 86 and 120 after acetylation for the whole plant essential oil (5) or rhizome essential oil (6), which suggested to us that substantial amounts of alcohols were present in the oils.

Rhizomes of *H. spicatum*, collected near Nainital at an elevation of 7500 ft, gave an essential oil whose gc/ms indicated the presence of at least 25 components including 1,8-cineole (29.7%), linalool (4.4%), and, not unexpectedly, several sesquiterpene alcohols that made up more than 40% of the oil. Fraction distillation of the oil, followed by one or more chromatographic methods, when

necessary, gave analytical samples of 1,8-cineole (9), (+)-linalool (9, 10), and five of the alcohols, which we identified as (-)- $\alpha$ -cadinol (11), (+)-elemol (12), (-)-*epi*-10- $\gamma$ -eudesmol (13), (+)- $\alpha$ -eudesmol (14), and (+)- $\beta$ -eudesmol (14) by means of their optical rotations and ir, <sup>1</sup>H-nmr, <sup>13</sup>C-nmr, and mass spectra.

Our <sup>13</sup>C-nmr spectrum of  $\beta$ -eudesmol and 10-*epi*- $\gamma$ -eudesmol are in complete agreement with the reported spectra (14, 15), but our spectrum of  $\alpha$ -eudesmol differs from that reported (14) in that we observed two signals for the diastereotopic methyl carbons at  $\delta$  27.6 and 26.8 ppm and not a single resonance at  $\delta$  27.2 ppm. The <sup>13</sup>C-nmr spectrum of  $\alpha$ -cadinol is given here for the first time; band assignments were made using chemical shift theory (16) and published spectra of similar compounds (17).

The composition of the essential oil from rhizomes of *H. spicatum* is summarized in Table 1 together with the reported findings of earlier workers (6-8). The large amount of sesquiterpene alcohols present in the oil clearly explains the high ester value after acetylation for the oil reported earlier (6) and probably accounts for most of the biological activity ascribed to the rhizomes and their extracts.

## EXPERIMENTAL

Capillary gc was carried out with a Hewlett Packard 5880 gas chromatograph using a 50 m

TABLE 1. Chemical Composition of Essential Oil from Rhizomes of *Hedychium spicatum*

	Garg <i>et al.</i> (6)	Dixit <i>et al.</i> (7)	Nigam <i>et al.</i> (8)	This work <sup>a</sup>
<b>Monoterpenes</b>				
$\Delta^3$ -carene . . . . .		1.4		
1,8-cineole . . . . .	56.2	37.2	27.1	29.7
<i>p</i> -cymene . . . . .		5.0	9.6	
limonene . . . . .		1.3	17.0	<sup>b</sup>
linalool . . . . .	6.8	18.0	16.6	4.4
$\beta$ -phellandrene . . . . .		4.5	7.0	
$\alpha$ -pinene . . . . .		1.4	1.8	<sup>b</sup>
$\beta$ -pinene . . . . .		1.4	4.5	<sup>b</sup>
terpinen-4-ol . . . . .				0.7
$\alpha$ -terpineol . . . . .	1.6		6.5	1.0
$\beta$ -terpineol . . . . .			1.8	
<b>Sesquiterpenes</b>				
(-)- $\alpha$ -cadinol . . . . .				5.3
$\beta$ -caryophyllene . . . . .	0.1	24.1	3.5	
$\beta$ -caryophyllene oxide . . . . .		0.5		
(+)-elemol . . . . .		4.2		8.5
(-)-10- <i>epi</i> - $\gamma$ -eudesmol . . . . .				5.1
(+)- $\alpha$ -eudesmol . . . . .				4.8
(+)- $\beta$ -eudesmol . . . . .				12.6
<b>Seven unknown alcohols</b>				
(C <sub>15</sub> H <sub>26</sub> O) . . . . .				6.2

<sup>a</sup>By normalization of capillary gc data. Some retention times (min) of interest:  $\alpha$ -cadinol, 99.02; elemol, 85.84; 10-*epi*- $\gamma$ -eudesmol, 86.28;  $\alpha$ -eudesmol, 97.55;  $\beta$ -eudesmol, 98.23 (see Experimental section for conditions).

<sup>b</sup>Total monoterpene hydrocarbons: 5.9%.

fused silica WCOT Carbowax column and a FI detector; conditions: initial temp 80° for 1 min, raised 1.0°/min to 180°, then isothermal for 30 min. Preparative gc was done with a Varian 200 gas chromatograph with a TC detector using a 10 ft × 1/4 in. stainless steel column packed with Chromosorb W AP (60-80 mesh) coated with 5% OV-101. Gc/ms was performed with a Hewlett Packard 5840A gas chromatograph interfaced with a Hewlett Packard 5985 mass spectrometer; the gc column was a 35-m fused silica DB5 column; conditions: initial temp 60° for 1 min, raised 2.5°/min to 135°, then 5°/min to 220°, then isothermal. Hplc was carried out with a home-made apparatus consisting of a Waters pump, a 10- $\mu$  Porasil column (25-cm × 9-mm), and a Perkin-Elmer LC-85 variable wavelength spectro-photometric detector set at 210 nm. Si gel (230-400 mesh), supplied by Sigma Chemical Co., and *n*-hexane-Et<sub>2</sub>O (7:3) were used for column chromatography. Ir spectra were recorded with a Beckman AccuLab 4 spectrophotometer. <sup>13</sup>C- and <sup>1</sup>H-nmr spectra were obtained with NT-200 and NT-360 spectrometers at the University of California, Davis, NMR Facility. High resolution electron impact mass spectra at 70 eV were obtained with a VG Analytical ZAB-HS mass

spectrometer at the Mass Spectrometry Laboratory, University of California, Davis.

**PLANT MATERIAL.**—*H. spicatum* was collected in July 1982, from Lariakanta in the vicinity of Nainital at an elevation of 7500 ft. Identity of the plant was confirmed by Y. P. S. Pangtey, Kumaun University, where herbarium samples (Nos. 3316 and 3317) have been deposited.

**ISOLATION OF ESSENTIAL OIL.**—The fresh, finely chopped rhizomes (18 kg) were subjected to steam distillation. The distillate was saturated with NaCl and extracted with petroleum ether, bp 60-80°. The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed with a rotary film evaporator at 45°. The residual oil weighed 54.0 g (0.3%).

**ISOLATION OF COMPONENTS.**—A 23.0-g aliquot of the oil was distilled through a B/R Model 24 spinning band distillation assembly using reflux ratio of 35-85 except during collection of the last fraction when a reflux ratio of 12 was used. The first fractions (2.75 g), bp 62° (18-20 torr), were nearly pure 1,8-cineole. The next several fractions (5.86 g), bp 62° (3 torr)-120° (2.7 torr), contained most of the (+)-linalool and

(+)-elemol in the oil; analytical samples were isolated by prep gc. The last fractions (2.85 g), bp 120-123° (2.7 torr), contained 26% (+)-elemol, 19% (-)-10-*epi*- $\gamma$ -eudesmol, and a total of 30% (-)- $\alpha$ -cadinol, (+)- $\alpha$ -eudesmol, and (+)- $\beta$ -eudesmol. The latter three alcohols made up ca. 80% of the 10.5-g distillation residue. An analytical sample of (-)-10-*epi*- $\gamma$ -eudesmol was obtained from an appropriate distillation fraction by column chromatography followed by hplc (7:3, *n*-hexane-Et<sub>2</sub>O). Analytical samples of the other three compounds were obtained from the residue by flash chromatography followed by preparative hplc (95:4:1, *n*-hexane-Et<sub>2</sub>O-MeCN).

<sup>13</sup>C-NMR SPECTRUM.—(-)- $\alpha$ -Cadinol:  $\delta$  (CDCl<sub>3</sub>) 135.0 (C<sub>4</sub>), 122.3 (C<sub>5</sub>), 72.4 (C<sub>10</sub>), 50.0 (C<sub>1</sub>), 46.7 (C<sub>7</sub>), 42.2 (C<sub>9</sub>), 39.8 (C<sub>6</sub>), 30.9 (C<sub>3</sub>), 25.9 (C<sub>11</sub>), 23.8 (C<sub>15</sub>), 22.7 (C<sub>8</sub>), 21.9 (C<sub>2</sub>), 21.1 (C<sub>12</sub>), 20.8 (C<sub>14</sub>), 15.1 (C<sub>13</sub>) ppm.

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#### LITERATURE CITED

1. "The Wealth of India," Vol. 5, CSIR Publications, New Delhi, 1959, p. 13.
2. R.N. Chopra, S.L. Nayar, and I.C. Chopra, "Glossary of Indian Medicinal

- Plants," CSIR Publications, New Delhi, 1956.
3. S.C. Sharma, J.S. Tandon, H. Uprety, Y.N. Shukla, and M.M. Dhar, *Phytochemistry*, **14**, 1059 (1975).
4. S.C. Sharma, Y.N. Shukla, and J.S. Tandon, *Phytochemistry*, **14**, 578 (1975).
5. A.K. Sinha and M.S. Mehra, *Indian Perfum.*, **21**, 129 (1977).
6. S.N. Garg, A.S. Shawl, and B.C. Gulati, *Indian Perfum.*, **21**, 79 (1977).
7. V.K. Dixit, K.C. Varma, and V.N. Vashist, *Indian J. Pharm.*, **39**, 58 (1977).
8. M.C. Nigam, M.S. Siddiqui, L.N. Misra, and T. Sen, *Parfuem. Kosmet.*, **60**, 245 (1979).
9. Y. Yukawa and S. Ito, "Spectral Atlas of Terpenes and the Related Compounds," Mirokawa Publishing Co., Inc., Tokyo, 1973.
10. "Sadtlter Standard <sup>13</sup>C-NMR Spectra," Sadtlter Research Laboratories, Philadelphia, 1976, #823C.
11. A.K. Borg-Karlson, T. Norin, and A. Talviti, *Tetrahedron*, **37**, 425 (1981).
12. E. Kleinpeter, M. Kretschmer, P.T. Son, and M. Muhlstadt, *Z. Chem.*, **22**, 261 (1982).
13. J.A. Marshall and M.T. Pike, *J. Org. Chem.*, **33**, 435 (1968).
14. G. Cordano, M.A. Merrien, J. Polonsky, R.M. Rabanal, and P. Varenne, *J. Indian Chem. Soc.*, **55**, 1148 (1978).
15. H. Itokawa, H. Morita, K. Watanabe, S. Mihashi, and Y. Iitaka, *Chem. Pharm. Bull. Japan*, **33**, 1148 (1985).
16. F.W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra," Wiley, New York, 1983, Chapter 2.
17. J.R. Williams and J.F. Callahan, *J. Org. Chem.*, **45**, 4475 (1980).

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