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HETEROCURVISTONE, A SESQUITERPENE WITH A 2-OXABICYCLO [2.2.2] OCTANE SKELETON

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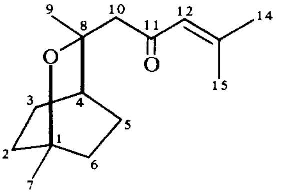
Key Word Index—*Heterotropa curvistigma*; Aristolochiaceae; sesquiterpene; heterocurvistone; 2-oxabicyclo [2.2.2] octane skeleton.

Abstract—A new sesquiterpene, heterocurvistone, has been isolated from *Heterotropa curvistigma* and shown to have the 2-oxabicyclo [2.2.2] octane skeleton.

In connection with our studies on asatone and isoasatone, we have continued searching for asatone-type neolignans in the Aristolochiaceae plants and we have isolated several new neolignans from *Heterotropa takaoi* [1, 2]. Further study on the MeOH extracts of *Heterotropa curvistigma*, which was already known to contain asatone [3], resulted in the isolation of a new sesquiterpene, named heterocurvistone, with a 2-oxabicyclo [2.2.2] octane skeleton, in addition to asatone and related, known neolignans [1]. In the present paper we describe the isolation and structure of heterocurvistone (1).

Fresh leaves and roots of the above plant (10 kg) collected at Shizuoka, late in April were homogenized with large volumes of MeOH at room temperature, left for a month and then filtered. The filtrate was concentrated under reduced pressure to give a greenish brown oil (308 g), which was further extracted with EtOAc. The EtOAc extract (49 g) was chromatographed on Si gel (Mallinckrodt, 100 mesh) (1350 g) using *n*-hexane–EtOAc (3:1) to give an oil (8.7 g), which was rechromatographed on Si gel (Mallinckrodt, 100 mesh) (160 g). After elution of 6-methoxysafrol and related aromatic compounds using $CHCl_3$, further elution with the same solvent afforded an oil (763 mg) which was further chromatographed on Si gel (Mallinckrodt, 100 mesh) (30 g) and eluted with $CHCl_3$–EtOAc (20:1) to give an almost colourless oil (190 mg). This oil was further purified by preparative TLC (Kieselgel PF_{254}; 1 mm; developed with $CHCl_3$; method of detection: UV light (254 nm); eluant: EtOAc) to afford a colourless viscous liquid of heterocurvistone (1) (50 mg), in 0.0005 % yield, with the following physical data: $[\alpha]_D^{24} - 49.5°$ (MeOH; *c* 1.05); ν_{max}^{film} 1680 and 1615 cm^{-1}; λ_{max}^{MeOH} 241 nm (ε 11 160); ^1H NMR (100 Mz, $CDCl_3$): δ 1.06 (3 H, *s*), 1.25–2.25 (9 H, complex), 1.34 (3 H, *s*), 1.88 (3 H, *s*), 2.11 (3 H, *s*), 2.69 (2 H, *s*) and 6.13 (1 H, *br. s*); MS (70 eV) *m/z* (rel. int.): 236 $[M^+]$ (1.4), 221 $[M^+ - Me]$ (7.6), 139 $[M^+ - C_6H_9O]$ (100), 95 (31.5), 83 (48.9) and 55 (25). (Found: *m/z* 236.17665; $C_{15}H_{24}O_2$ requires: *m/z* 236.17762.)

In addition to the IR and UV spectra, the ^1H NMR signals at δ 1.88, 2.11, 2.69 and 6.13 together with the fragment peak at *m/z* 139 strongly suggest that heterocurvistone has a partial structure $+CH_2$—$COCH{=}C(Me)_2$. Furthermore, it has two tertiary Me groups and one ether oxygen atom. Finally, the structure



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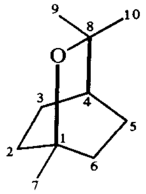

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Table 1. ^{13}C NMR spectral data of heterocurvistone (1) and cineol (2)

C atom	Heterocurvistone (1)*	Cineol (2)†
1	69.7 *s*	69.6 *s*
2	31.6 *t*	31.5 *t*
3	23.0 *t* or 22.4 *t*	22.8 *t*
4	30.5 *d*	32.9 *d*
5	22.4 *t* or 23.0 *t*	22.8 *t*
6	31.6 *t*	31.5 *t*
7	27.4 *q* or 27.6 *q*	27.5 *q*
8	75.5 *s*	73.5 *s*
9	27.6 *q* or 27.4 *q*	28.8 *q*
10	55.4 *t*	28.8 *q*
11	199.0 *s*	
12	125.1 *d*	
13	154.0 *s*	
14	26.6 *q*	
15	20.6 *q*	

* The ^{13}C NMR spectrum (25 MHz) of **1** was measured in $CDCl_3$ using TMS as the internal standard.

† See ref. [3].

of heterocurvistone (**1**) was established on the basis of an exhaustive comparison of the ^{13}C NMR spectra between **1** and cineol (**2**) [4, 5], as seen in Table 1, although the absolute configuration of **1** remains unsettled.

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