

confirmed that the compounds isolated by preparative GLC were not thermally altered during the separation, by means of TLC and/or IR.

α -[6] and β -Bisabolol [7], *t*-cadinol [8], cubenol [9], *t*-muurolol [8], (-)-junenol [10], nerolidol, (+) cadinenol (1) [11], and epicubenol (2) [9] were isolated and identified by means of spectral data, GLC (*R*_t) and other physico-chemical properties, along with the above mentioned components.

Among them, (1) (mp at 75°C, [α]_D = +5.9) and (2) (liquid, [α]_D = -89.6) had almost identical IR-, NMR- and MS, but the ¹³C-NMR-spectrum of (1) differs from that of (2); the main difference being a signal at 29.7 ppm in the ¹³C-NMR-spectrum of (1) which is not found in that of (2).

Cadinenol has been isolated by several researchers [10,12-14], but there are slight differences in [α]_D among these isolates. Tomita and Hirose obtained a crystalline sesquiterpene alcohol from *Juniperus rigida* (mp 75°, [α]_D ± 0), the IR- and NMR-spectra of which were identical with those of epicubenol and cadinenol, and they identified it as (±) epicubenol [15]; in that report, they also said that it was identical with cadinenol.

From our experiments, however, we conclude that cadinenol is not identical with (±) epicubenol by reason of separation of (1) and (2) from each other chromatographically and by their having different ¹³C-NMR-spectra.

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ASATONE IN PLANTS OF THE ARISTOLOCHIACEAE

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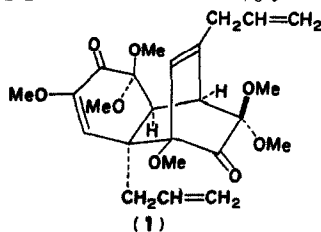
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Key Word Index—*Asarum*, *Asiasarum* and *Heterotropa* spp; Aristolochiaceae; asatone.

Chemotaxonomic studies on species of *Asarum*, *Asiasarum* and *Heterotropa* have been extensively carried out particularly by Saiki and his co-workers [1]. In most cases, however, chemical constituents have been examined in steam-distillates of the fresh or air-dried leaves of the plant. Recently, we examined the chemical components in *n*-hexane extracts of *Asarum taitonense* Hayata (Taiton Kanaoi in Japanese) growing in Taiwan, and isolated two novel compounds, asatone (1) [2] and isoasatone [3], in ca 0.2 and 0.001% yields, respectively.



* Fresh leaf material. The other air-dried materials were kindly supplied by Prof. Y. Saiki (Shizuoka College of Pharmacy), and their sources and chemical components of the steam-distillates are cited in reference [1]. § Collected in Gifu-ken in middle of September. || Collected in Aichi-ken in middle of September. † Collected in Aichi-ken late in August.

From the chemotaxonomic view point, it seemed useful to examine other species of *Asarum*, *Asiasarum* and *Heterotropa*, to see if they also contain asatone (1). We examined eighteen species, and isolated asatone (1) from four, (Group A below), by the following general procedure. Fresh leaves of *Heterotropa takaoi* F. Maekawa (200 g) were disintegrated into *n*-hexane (500 ml × 2) and left at room temp. for 1 week, and the filtrate concentrated under reduced pressure to yield a yellow oil, which on treatment with small amounts of *n*-hexane afforded white crystals (105 mg) of asatone (mp, IR and MS). The mother liquor was concentrated and subjected to preparative TLC (Kieselgel 60 PF₂₅₄) using *n*-hexane-EtOAc (3:1) to give three main compounds, safrol (20 mg), elemicin (73 mg) and asatone (113 mg). The leaf residue was further extracted with MeOH (500 ml × 2) at room temp. for a week to give a greenish-brown oil (350 mg), which by preparative TLC gave further quantities of the three compounds. In total, safrol, elemicin and asatone (1) were obtained from the fresh plant in 0.018, 0.066 and 0.15% yields, respectively.

The 14 other plants in which no asatone could be detected are shown in Group B.

Group A: *Heterotropa nipponica* var. *brachypodium* F. Maekawa (0.18%)*§; *H. takaoi* F. Maekawa (0.15%)*||;

H. curvistigma F. Maekawa (0.38%); *H. hexaloba* var. *perfecta* F. Maekawa (0.30%).

Group B: *Asarum caulescens* Maxim**†; *Asarum hirsutisepalum* Hatsushima**; *A. yakusimense* Masam**; *Asiasarum heterotropides* var. *seoulense* F. Maekawa; *A. sieboldii* F. Maekawa; *Heterotropa albivenium* F. Maekawa; *H. asaroides* Morr. et Decne; *H. crassa* F. Maekawa; *H. kiusiana* F. Maekawa; *H. megacalyx* F. Maekawa; *H. muramatsui* F. Maekawa; *H. nipponica* F. Maekawa; *H. savatieri* F. Maekawa; *H. tamaensis* F. Maekawa.

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** Collected in Yakushima in middle of November.

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TRITERPENES FROM LATEX OF *EUPHORBIA BALSAMIFERA*

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Key Word Index—*Euphorbia balsamifera*; Euphorbiaceae; tabaiba dulce; germanicol; germanicone; lupeol; lupenone; β -amyrin; cycloartenol; dihydroagnoterol; cycloartanone.

Plant. *Euphorbia balsamifera* Ait. **Source:** Collected on the coast of Guia de Isora, Tenerife, Canary Isles. **Previous work:** germanicol, cycloartenol and lanosterol [1–3].

Present work. The unsaponifiable of the latex (11.) was chromatographed on silica gel, yielding the following compounds which were characterized by their physical and spectroscopic data: *germanicol* (3.1 g), *germanicone* (89 mg), *lupeol* (4.5 g), *lupenone* (38 mg), β -*amyrin* (140 mg) and *cycloartenol* (300 mg) which were identified by comparison with authentic samples; *dihydroagnoterol* (80 mg), obtained as alcohol, was characterized as the acetate, mp 165–171° (MeOH), $[\alpha]_D^{25} +62$ (CHCl₃; *c* 0.76); its UV spectrum [λ_{max} (EtOH) nm (log ϵ): 236 (3.89), 243 (3.95), 253 (3.79)] was in agreement with an homoanular dienic system which was corroborated by the NMR (CDCl₃) signal at δ 5.74 (2H, *m*, *W*_{1/2} 15 Hz);

cycloartanone (50 mg), isolated for the first time in nature, mp 95–99° (MeOH), IR ν_{max} (CHCl₃) cm⁻¹: 3020, 1695; MS (probe) 70 eV *m/e* (rel. int.): 426 M⁺, 411 (M⁺–15; 100), 355, 342, 313, 288, 257, 245, 231, 175, 163, 161, 159, displaying characteristic fragments of tetracyclic triterpenes with a cyclopropane ring between C-9 and C-10 [4,5]; NMR (60 MHz, CDCl₃): δ 0.60 (2H, *dd*); its IR and NMR spectra were superimposable with those of a synthetic sample.

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TRITERPENOIDS OF THE STEMS OF SIX
CASTANOPSIS SPECIES OF HONG KONG

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Key Word Index—*Castanopsis concinna*, *C. cuspidata*, *C. eyrei*, *C. fabri*, *C. fissa* and *C. hickelii*; Fagaceae; triterpenoids; rearranged oleananes, lupanes, hopanes and ursanes; steroids.

Plants. *Castanopsis concinna* A. DC., *C. cuspidata* (Thunb.) Schky., *C. eyrei* (Champ.) Tutch., *C. fabri* Hance, *C. fissa* Rehd. and Wils., and *C. hickelii* A. Camus.