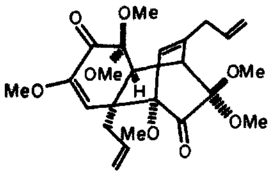
Table 1. Presence of asatone in *Asarum* subgenus Heterotropa

	Asatone content*
Section Aschidasarum	
A. hexalobum F. Maekawa	0.30
A. hexalobum var. *perfectum* F. Maekawa [2]	0.28
A. asperum F. Maekawa	0.42
A. oblongum F. Maekawa	0.41
Section Euheterotropa (= Heterotropa)	
A. tamaense var. tamaense	0.24
A. tamaense var. *muramatsui*	0.28
A. curvistigma F. Maekawa [2]	0.34
A. unzen (F. Maekawa) Kitamura	0
A. asaroides (Morr. et Decne) Makino	0
A. satsumense F. Maekawa	0
Section Bicornes	
A. nipponicum var. F. Maekawa *nipponicum*	0.25
A. nipponicum var. *brachypodion* F. Maekawa [2]	Contain asatone (not investigated in the present work)
A. takaoi F. Maekawa var. *takaoi* [2]	

* Percentage of the fresh weight of the total plant (leaves and roots).



Asatone

Present work. Fresh leaves and roots of the above 11 taxa were minced separately and extracted with *n*-hexane. Concentration of the extractives in vacuum gave oily substances which crystallized when cooled in the refrigerator. Chromatography of the substances over Si gel using *n*-hexane–ethylether (2:1) gave white crystalline solids mp 100–101° (from MeOH), $C_{24}H_{32}O_8$ (Found: C64.27; H7.12; O 28.69. Calcd C 64.27; H 7.14; O 28.59. MS *m/e* (rel. int): 448 (M^+ 3.7), 416 (32.2), 384 (34.6), 343 (20.3), 224 (40.0), 223 (14.9), 193 (13.9), 181 (25.4), 105 (base peak). UV λ_{max}^{EtOH} nm: 275 (ϵ 6730). Ir ν_{max}^{CCl} 4 cm^{-1}: 1750, 1722, 1640, 1145, 1130, 1080, 1050, 914, 816. These spectral data are in good agreement with those of asatone. The contents of asatone in the 11 taxa are shown in Table 1. The contents of asatone in the *n*-hexane extractives of the plants (leaves and roots) were calculated from the peak areas obtained with high speed liquid chromatography employing two GPC columns of Shodex A802 (porous polymer of divinylbenzene) (500 × 8 mm) using tetrahydrofuran as the eluting solvent. More recently, Yamamura [2] reported that only four species (*A. nipponicum* var. *brachypodion* F. Maekawa, *A. hexalobum* var. *perfectum* (F. Maekawa), *A. curvistigma* F. Maekawa, *A. Takaoi* F. Maekawa var. *Takaoi*) *growing in the central part of Japan contained asatone in their* *n*-hexane extractives. However, the results reported now, show that asatone is more wide spread in *Asarum sensu lato*. It occurs in several sections of the subgenus Heterotropa (Table 1). It is of interest that of the taxa belonging to the section Heterotropa some contain much asatone mainly in the roots (Table 1) and others have no asatone . The latter plants grow in the most western parts of the country (Kyushu: Western distinct of Honshu) and the former grow in the central distinct of Japan. This correlation between plant distribution and Asatone content seems to hold only for section Heterotropa, however. The asatone-containing taxa of section Aschidasarum have a western distribution (Kyushu, Shikoku, Western Honshu) similar to the asatone-free taxa of section Heterotropa.

Acknowledgements—We thank Dr. Isamu Hiura (The Osaka Museum of Natural History) for identification of the plants.

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A NEW MONOTERPENE TRIOL FROM *ZANTHOXYLUM BUDRUNGA**

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(*Received* 3 *February* 1976)

Key Word Index—*Zanthoxylum budrunga*; Rutaceae; 1S, 2S, 4S-trihydroxy-*p*-menthane; synthesis; 1S, 2R, 4S-trihydroxy-*p*-menthane.

Although some diols and diol ethers [1] have been isolated from nature, trihydroxy compounds are quite rare. In this paper we report the isolation and structural elucidation of a new monoterpene triol occurring in the volatile oil from *Zanthoxylum budrunga* fruits.

The volatile oil of *Z. budrunga* on repeated column chromatography over Si gel yielded a crystalline compound **1**, mp 171.5°, from EtOAc eluates. The compound analysed for $C_{10}H_{20}O_3$, M^+ 188 and preliminary investigation showed the presence of three OHs. It formed a

Table 1. PMR (C_5D_5N and $CDCl_3$) of 1

No.	$CDCl_3$	C_5D_5N δ values	Δ	Multiplicity	Protons
1	0.89	1.07	0.18	*d*, $J = 6$ Hz	Me Me > CH—
2	1.30	1.60	0.30	S	Me—C— OH
3	3.50	4.50	0.55	Broad singlet $W_{H1/2} = 6.75$ Hz	H—C—OH

Table 2. PMR (C_5D_5N and $CDCl_3$) 100 MHz of 2

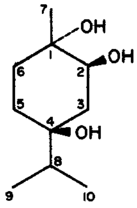
No.	C_5D_5N	$CHCl_3$ δ values	Δ	Multiplicity	Assignment
1	1.15	0.97	0.18	6, *d*, $J = 6$ Hz	Me Me > CH
2	1.59	1.27	0.32	3, *S*.	Me—C— OH
3	4 41	3.79	0.62	1, *q*, $J_{AX+BX} = 14$ Hz	H—C—OH

monoacetate with C_5H_5N and Ac_2O at room temp. mp 120–121°, $C_{12}H_{22}O_4$, M^+ 230 and a triacetate was obtained under reflux condition mp 96–97°, $C_{16}H_{26}O_6$ M^+ 314. IR of 1 showed absorption at 3300, 1380, 1365, 1260, 1140, 1065, 1030, 970, 875 and 750 cm^{-1} and that of the monoacetate gave bands at 3590 and 1695 cm^{-1} showing unacetylated hydroxyls. IR of 1 triacetate showed absorption at 1730 cm^{-1} due to the carbonyl of acetates. The PMR spectra of 1 was taken in C_5D_5N and $CDCl_3$ to determine the pyridine shifts [2] and the assignments of the various protons are given in Table 1.

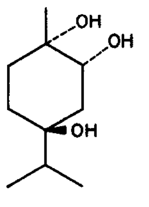
The probability of an OH at C-8 is ruled out as the isopropyl Mes are located a δ 1.07 (C_5D_5N) as a doublet (J 6 Hz). The C-1 Me as a singlet at δ 1.60 (C_5D_5N) indicate the presence of an-OH at C-1. A second tertiary OH can be placed at C-4.

The third OH is either at C-2 or C-3 because the acetate shows a shift of 1.47 ppm (3.50 → 4.97 $CDCl_3$) indicative of a proton geminal to acetate. Had this proton been at C-3, there should have been a 1:3 diaxial interaction with one of the Mes at C-8 irrespective of its α or β nature. This interaction would have resulted in a large C_5H_5N shift [2], which was not found with 1. Therefore, the third OH is at C-2. This is supported by the fact that the C-1 Me is more downfield than the geminal OH indicating a 1:2 vicinal interaction with the C-2 OH [2].

To fix the stereochemistry of the three OH's a similar (not identical) compound with *cis* C-1 and C-2 OH groups was synthesized. For this, terpinen-4-ol was subjected to OsO_4 oxidation [3] and after usual work up a major compound 2 mp 96–99° was formed, which was assigned the structure B. The PMR of 2 (Table 2) showed a marked difference in the position and complexity of the C-2 proton. From the molecular model of 1, it is clear that when the C-2 OH is β, the C-2 proton bisects the C-3 methylenes with the result that C-2 proton appears as a broad singlet at δ 4.05 ($W_{H_{1/2}} = 6.75$ Hz). In 2, this proton appears at δ 4.41 (C_5D_5N) as a four line quartet typical for X protons of an ABX system. This is possible only when the C-2 OH is α.



A



B

Thus 1 is 1S, 2S, 4S-trihydroxy-*p*-menthane (A) and 2 is 1S, 2R, 4S-trihydroxy-*p*-menthane (B). MS of 1 showed fragments at *m/e* 170, 152, 145, 127, 117, 109, 99 and 81 which are consistent with the structure proposed.

The structure was further confirmed by synthesising 1 from terpinen-4-ol with H_2O_2 and HOAc. This triol had mp 172° and mmp undepressed with 1. IR spectra of this compound was also superimposable with 1. Garside *et al.* [4] have also reported a triol mp 172° as a synthetic compound prepared by the oxidation of sabinol and terpinen-4-ol and this compound would also appear to be identical with 1.

Acknowledgements—The authors thank Mr. Eric Underwood, Exeter for the PMR and Dr. Y. V. Subbarao, RRL, Hyderabad for MS.

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*The paper was presented in the Symposium on Isoprenoids: Chemistry and applications, Nov. 24–26, 1975, Baroda, India.