

Table 1. Fatty acid composition of triglycerides, cyanolipids and the cyanolipid fractions of *Sapindus emarginatus* seed oil

| Lipid                        | Concn<br>wt % | Fatty acid, (mol %) |      |      |       |      |      |       |
|------------------------------|---------------|---------------------|------|------|-------|------|------|-------|
|                              |               | 16:0                | 18:0 | 18:1 | 18:2  | 20:0 | 20:1 | 22:0  |
| Triglycerides                | 82.0          | 8.8                 | 3.0  | 64.7 | 2.9   | 11.8 | 8.8  | —     |
| Cyanolipids                  | 16.0          | 3.9                 | 1.2  | 49.8 | Trace | 33.2 | 11.9 | Trace |
| Argentation<br>TLC fractions |               |                     |      |      |       |      |      |       |
| First                        | 26.8          | —                   | —    | 55.0 | —     | —    | 45.0 | —     |
| Second                       | 67.7          | 2.8                 | —    | 49.2 | —     | 46.5 | —    | 1.5   |
| Third                        | 5.5           | 46.8                | 3.3  | —    | —     | 49.9 | —    | —     |

sanoic acid occurs in the cyanolipids than in the triglycerides.

MS of the methoxy derivatives [9] gave peaks at *m/e* 157, 171, 201, 215, 229 and 243. These showed the presence of a double bond at the 9 position from the terminal Me group in both the 18:1 and 20:1 acids.

#### EXPERIMENTAL

Oil was Soxhlet extracted from *S. emarginatus* kernels with PE. TLC was carried out on 0.25 mm Si gel G layers using both C<sub>6</sub>H<sub>6</sub> and Et<sub>2</sub>O-PE-HOAc (15:85:1). Cyanolipids were isolated on 1 mm Si gel G layers using 15% Et<sub>2</sub>O in PE. Cyanolipids were fractionated on 0.5 mm layers of 5% AgNO<sub>3</sub>-impregnated Si gel G using CCl<sub>4</sub>-CHCl<sub>3</sub>-EtOH (50:50:1), and detected with ethanolic 2', 7'-dichlorofluorescein and estimated gravimetrically. The Me esters were prepared using 1% NaOMe in MeOH. Total Me esters from the triglycerides and the monoene Me esters from the cyanolipids, isolated by AgNO<sub>3</sub> TLC were converted to methoxy derivatives and purified [9]. The PMR spectra were measured in CCl<sub>4</sub> at 60 MHz.

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#### ASATONE IN ASARUM (ARISTOLOCHIACEAE)

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**Key Word Index**—*Asarum*; Heterotropa; Aristolochiaceae; *Asarum hexalobum*, *A. asperum*, *A. oblongum*, *A. tamaense*, *A. tamaense* var. *muramatsui*, *A. nipponicum*; *n*-hexane extractives; asatone.

*Plants and source.* *Asarum hexalobum* F. Maekawa and *Asarum asperum* F. Maekawa collected in May at Hiroshima Prefecture. *Asarum oblongum* F. Maekawa collected in July at Shimane and Tottori. *Asarum tamaense* Makino collected in December at Tokyo. *Asarum tamaense* var. *muramatsui* (Makino) Sugimoto and *Asarum nipponicum* F. Maekawa var. *nipponicum* collected in December at Shizuoka. *Asarum hexalobum* var. *perfectum* F. Maekawa and *Asarum satsumense* F. Maekawa collected in January at Kagoshima. *Asarum unzen*

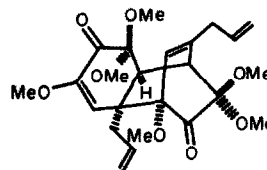
(F. Maekawa) Kitamura collected in December at Saga. *Asarum asaroides* (Morr. et Decne) Makino collected in May. *Asarum curvistigma* F. Maekawa collected at Yamanashi in December. *Uses.* Medicinal. *Previous work.* Recently Yamamura *et al.* [1,2] isolated a new neolignan, Asatone from *n*-hexane extractives of *A. taitonense* Hayata growing in Formosa and from *A. nipponicum* var. *brachypodion*, *A. takaoi* F. Maekawa var. *takaoi*, *A. hexalobum* var. *perfectum*, *A. curvistigma* F. Maekawa of Japan.

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

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

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

**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-ethyl ether (2:1) gave white crystalline solids mp 100–101° (from MeOH), C<sub>24</sub>H<sub>32</sub>O<sub>8</sub> (Found: C 64.27; H 7.12; O 28.69. Calcd C 64.27; H 7.14; O 28.59. MS *m/e* (rel. int): 448 (M<sup>+</sup> 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<sub>max</sub><sup>EtOH</sup> nm: 275 (ε 6730). IR ν<sub>max</sub><sup>CCl<sub>4</sub></sup> cm<sup>-1</sup>: 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



Asatone

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*.

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A NEW MONOTERPENE TRIOL FROM *ZANTHOXYLUM BUDRUNGA*\*

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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<sub>10</sub>H<sub>20</sub>O<sub>3</sub>, M<sup>+</sup> 188 and preliminary investigation showed the presence of three OHs. It formed a