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# SESQUITERPENES FROM TAIWANESE LIVERWORTS

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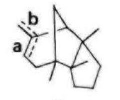
Ten Taiwanese leafy liverworts of six genera were examined for their sesquiterpene hydrocarbons (Table 1). Among these, *Bazzania angustifolia* (Wu & Liu 1983), *B. fauriana* (Wu et al. 1982a), *Plagiochila kahsiana* (Wu et al. 1982b), *Schistochila rigidula* (Wu et al. 1983), *Scapania ornithopodioides* (Wu et al. 1982c) and *S. robusta* (Wu & Huang 1981, Wu & Lee 1983) have been reported previously, but newly identified compounds are added in the present paper and are printed in bold faces in Table 1. Main components of each species are marked with an asterisk.

In this paper, I will discuss several interesting points found in the chemical studies of these ten Taiwanese liverworts.



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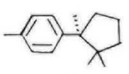

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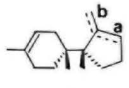

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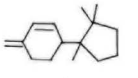

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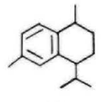

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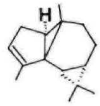

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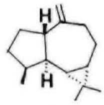

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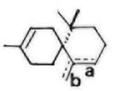

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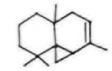

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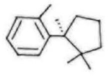

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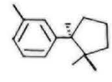

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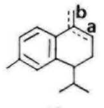

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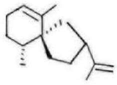

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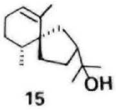

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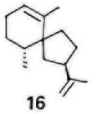

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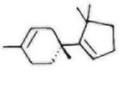

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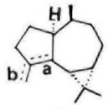

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## RESULTS AND DISCUSSION

### 1. Angustifolene (4), a new sesquiterpene, found in every Taiwanese liverwort examined

As one can see from Table 1, four sesquiterpenes, i.e., β-barbatene (**1b**), cuparene (**2**), β-bazzanene (**3b**) and angustifolene (**4**), occur in every Taiwanese liverwort examined. Among them, the former three are common liverwort components. The last one, angustifolene (**4**), however, is a new sesquiterpene. Its percentage in each oil is always minor, but it is easily recognized due to its particularly late elution on nonpolar GC phases and its unique MS fragments (Wu et al. 1983). The structure of angustifolene shown as **4**, is tentatively assigned and a detailed proof will be reported later.

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TABLE 1. Sesquiterpenes from Taiwanese liverworts.

| | Species | Collected site and data | Sesquiterpenes detected[#] |
|---|---|---|---|
| 1. | *Bazzania angustifolia* | Yuen-yang Lake, Ilan, June 30, 1980 | α-barbatene (**1a**), thujopsene (**10**), isobazzanene (**17**), β-barbatene (1**b**), **$\mathrm{M}^{+}$204** (41)[†], β-chamigrene (**9b**), cuparene (**2**), α-bazzanene (**3a**), β-bazzanene (**3b**)*, angustifolene (**4**) |
| 2. | *Bazzania fauriana* | Yuen-yang Lake, Ilan, June 30, 1980 | **α-copaene,** α-barbatene, **isobazzanene, $\mathrm{M}^{+}$204** (122), β-barbatene, **ar-curcumene,** β-chamigrene, cuparene, **α-chamigrene** (**9a**), **calamenene (6), α-bazzanene,** β-bazzanene*, **angustifolene, $\mathrm{M}^{+}$202 (119), calacorene (13)** |
| 3. | *Bazzania tridens* | Ali Shan, Chiayi, Sept. 7, 1982 | $\mathrm{M}^{+}$204 (119)*, anastreptene (**7**), $\mathrm{M}^{+}$204 (161)*, $\mathrm{M}^{+}$204 (93), β-barbatene*, α-barbatene, $\mathrm{M}^{+}$204 (119), $\mathrm{M}^{+}$204 (119), $\mathrm{M}^{+}$204 (119), cuparene, α-bazzanene, β-bazzanene, angustifolene, $\mathrm{M}^{+}$202 (132, 145) |
| 4. | *Mastigophora diclados* | Yuen-yang Lake, Ilan, Jan. 17 & Dec. 24, 1982 | anastreptene, longifolene, thujopsene, β-barbatene, α-patchoulene, $\mathrm{M}^{+}$202 (132), isocuparene (**11**)*, herbertene (**12**), cuparene, $\mathrm{M}^{+}$202 (132), bicyclogermacrene (**5**)?, β-bazzanene, calamenene, $\mathrm{M}^{+}$204 (161), angustifolene, $\mathrm{M}^{+}$202 (187), α-calacorene, β-calacorene, $\mathrm{M}^{+}$202 (147), $\mathrm{M}^{+}$202 (147) |
| 5. | *Mylia nuda* | Yuen-yang Lake, Jan. 17, 1982 | $\mathrm{M}^{+}$204 (161), δ-elemene, $\mathrm{M}^{+}$204 (189), $\mathrm{M}^{+}$204 (161), $\mathrm{M}^{+}$204 (189)*, cuparene*, $\mathrm{M}^{+}$204 (107), β-bazzanene*, calamenene, angustifolene |
| 6. | *Plagiochila kahsiana* | Yuen-yang Lake, June 30, 1980 | anastreptene*, $\mathrm{M}^{+}$204 (105)*, thujopsene*, aromadendrene (**8**), β-barbatene, β-chamigrene, β-selinene, α-selinene, cuparene, calamenene, β-bazzanene, **angustifolene** |
| 7. | *Schistochila rigidula* | Yuen-yang Lake, June 30, 1980 | anastreptene, α-barbatene, $\mathrm{M}^{+}$204 (107, thujopsene, aromadendrene*, β-barbatene*, β-chamigrene, $\mathrm{M}^{+}$204 (105), cuparnene, β-bazzanene*, angustifolene |
| 8. | *Scapania glaucoviridis* | Ali Shan, Chiayi, Sept. 7, 1982 | $\mathrm{M}^{+}$204 (105), δ-elemene, β-barbatene, $\mathrm{M}^{+}$204 (161), bicyclogermacrene?*, cuparene*, β-bazzanene, calamenene, $\mathrm{M}^{+}$204 (93), angustifolene |
| 9. | *Scapania ornithopodioides* | Yuen-yang Lake, June 30, 1980 & Jan. 17, 1982 | anastreptene, cyclosativene, β-elemene, **α-gurjunene (18b), α-barbatene,** β-farnesene, **β-gurjunene (18b),** $\mathrm{M}^{+}$204 (161), aromadendrene*, β-barbatene, ar-curcumene, selina-4, 11-diene, α-farnesene, β-chamigrene, |

TABLE 1. (Continued).

| Species | Collected site and date | Sesquiterpenes detected# |
|---|---|---|
| | | β-selinene*, α-selinene*, cuparene, $M^+$204 (93), β-bazzanene, **angustifolene**, calacorene |
| 10. *Scapania robusta* | Ali Shan, Chiayi, March 10, 1979 & March 19, 1981 | anastreptene, longifolene, **β-gurjunene**, aromadendrene, β-barbatene, selina-4, 11-diene, α-amorphene, **$M^+$204** (147)*, spirovetivene (**14**)*, cuparene, β-bazzanene, angustifolene |

# Sesquiterpenes are listed according to the GC elution order on the following liquid phases: SF-96 – species 1, 2, 6, 7, 9, 10; CP Sil-5 – species 3, 4; OV-101 – species 5, 8.

† Unidentified compound with the molecular ion as shown; number in parentheses is the base peak of this unidentified compound.

* Major components of the hydrocarbon fraction of the listed species.

The GC Kovats' indices (on Apiezon L, SF-96 and Carbowax-20M) of angustifolene (**4**) are fairly consistent with those of an unknown component from European *Bazzania trilobata* (Andersen et al. 1977). Asakawa et al. also reported a late eluted unknown sesquiterpene of $M^+$ 204 (base peak 69) from both Japanese *Bazzania tricrenata* and *B. trilobata* (Asakawa et al. 1981). Since the most intense MS fragments of angustifolene (**4**) are m/z 69 and/or 111, the above-mentioned unknown sesquiterpene from the two Japanese *Bazzania* species is very likely to be angustifolene (**4**). Hence angustifolene (**4**) seems to be a common constituent of universal liverworts and is not just produced by Taiwanese liverworts.

2. Any bicyclogermacrene (**5**) in Taiwanese liverworts?

The sesquiterpene constituents of Japanese *Bazzania tridens* were previously investigated (Toyota et al. 1981). They found bicyclogermacrene (**5**), α-barbatene (**1a**), β-barbatene (**1b**), β-bazzanene (**3b**), calamenene (**6**) and cuparene (**2**) in this species. In the present study, the results are more or less along the same line except that bicyclogermacrene (**5**) and calamenene (**6**) are not observed. Bicyclogermacrene (**5**) has been found in many liverworts and is an important precursor for various types of sesquiterpenes (Matsuo 1982). Nevertheless, this component has not been definitely identified in any of the Taiwanese liverworts examined. In *Mastigophora diclados* and *Scapania glaucoviridis*, the presence of bicyclogermacrene (**5**) was suspected based on the GC/MS analyses of these liverwort oils. In order to confirm the identity of this compound, further isolation or a comparison with authentic sample is necessary.

3. Aromadendrene (**8**) found in four of the ten species studied

In these ten liverworts studied, besides the four sesquiterpenes mentioned in the biginning of this section, several other components also have been found quite common. They are: anastreptene (**7**), aromadendrene (**8**), α-barbatene (**1a**), calamenene (**6**), β-chamigrene (**9b**) and thujopsene (**10**), Aromadendrene (**8**) was only reported once

(Matsuo et al. 1981a) as a constitutent of liverwort before our findings. It not only occurs in four Taiwanese species, it is also the most abundant component in *Scapania ornithopodioides* (Wu et al. 1982c). On the other hand, aromadendrene (**8**) was previously reported to be one of the thermal isomerized products from bicyclogermacrene (**5**) during either column chromatography on silica gel or gas chromatography at high injection port and detector temperatures (>160°C) (Maarse & van Os 1973, Malingré & Maarse 1974). Thus in order to clarify whether our aromadendrene (**8**) was derived from bicyclogermacrene (**5**) during analysis, the following treatment was carried out. The crude oil of *Scapania ornithopodioides* was quickly filtered through a 2.3 cm of commercial SEP-PAK silica column to remove the most polar fraction. The filtrate was then analyzed on GC/MS at temperatures of injection port 160°C and column 50°C with a programming rate of 2°C/min. All peaks of sesquiterpene hydrocarbons eluted from the FSOT OV-101 column within 12 min. and below column temperature of 74°C. In this manner, aromadendrene (**8**) was still observed as the largest peak and no bicyclogermacrene (**5**) could be detected. Therefore, it supports that aromadendrene (**8**) is synthesized enzymatically in these Taiwanese liverworts.

4. New isomer of cuparene (**2**) found in *Mastigophora diclados*

The major sesquiterpene of the rather primitive liverwort *Mastigophora diclados* is a new isomer of cuparene (**2**), named isocuparene (**11**). Although it had a high percentage (~60%) in the hydrocarbon fraction, the plant itself produced very small amount of hydrocarbons unfortunately. The structure **11** of this compound was assigned on the basis of its NMR spectrum ($\delta$ 0.57, 1.08, 1.27 & 2.33, 4 Me's; 7.11 & 7.33, 4 H's) which closely resembled those of cuparene (**2**) (Matsuo et al. 1971) and herbertene (**12**) (Matsuo et al. 1981). Other spectral data of isocuparene (**11**) will be published elsewhere. Another interesting feature of *M. diclados* is that this species, besides the major component, also synthesized quite a number of other minor aromatic sesquiterpenes, such as herbertene (**12**), cuparene (**2**), calamenene (**6**), $\alpha$- and $\beta$-calacorenes (**13**) as well as five unidentified ones ($M^+$ 202).

5. A spirovetivene from *Scapania robusta*

The major hydrocarbon of *Scapania robusta* was identified as spirovetivene (**14**) and its absolute configuration was suggested on the basis of chiroptical data (Wu & Lee 1983). Spirovetivene (**14**) actually possesses the same structure as the diene from a natural agrospirol (**15**) (Varma et al. 1965). Bheemasankara Rao et al. (1982) isolated a compound from higher plants named premnaspirodiene (**16**) which was also claimed to have the same IR and NMR characteristics as the diene from agarospirol (**15**). In any case, spirovetivene (**14**) from *S. robusta* would be the first instance of this type of spiroskeleton sesquiterpene produced by liverworts.

## EXPERIMENTAL

GC, GC/MS and spectral analyses were performed in the same manner as described in previous papers (Wu et al. 1982c, 1983, Wu & Lee 1983).

Extraction and identification of sesquiterpene hydrocarbons. Each sample of the airdried material was extracted with n-hexane for weeks after freezing with liquid $N_2$. The crude extract was passed through a short silica gel column for GC and GC/MS analyses. The rest extract was chromatographed over silica and $AgNO_3$-impregnated silica using an n-hexane/benzene/EtOAc gradient. Hydrocarbon fractions collected from chromatography were again analyzed with GC and GC/MS. Major components which could be isolated were identified by NMR spectra. Minor components were assigned by comparison of their GC Kovats' indices and their MS data with those of authentic samples and/or published information. Structures of new compounds were elucidated on the basis of mainly NMR abd MS data and simple chemical transformations. The results and the collection site and date of each species are compiled in Table 1.

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