ENT-ROSA-5,15-DIENE, A DITERPENE HYDROCARBON IN CRYPTOMERIA LEAF OIL

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Key Word Index—Cryptomeria japonica; C. fortunei; Taxodiaceae; diterpene hydrocarbons; ent-rosa-5,15-diene.

Abstract—Cryptomeria trees have been analysed which have ent-rosa-5,15-diene as the main diterpene in the leaf oil.

INTRODUCTION

It is believed that ent-kaurene [1], phyllocladene [2], and sclarene [3] or ent-sclarene [4] are the main alternative diterpene hydrocarbons of Cryptomeria leaf oil accompanied by ca 1% of hydrocarbon which has the same GC retention time as the other hydrocarbon. However, the coexistence of comparable amounts of ent-kaurene and phyllocladene [3], and ent-kaurene and ent-sclarene [5] was reported. We found some trees of Cryptomeria having ent-rosa-5,15-diene [6, 7] (1) as the main diterpene or one of the dual components.

RESULTS AND DISCUSSION

Two C. fortunei (Liu Shan) trees, one having ent-kaurene, phyllocladene, rimuene and 1 (10, 14, 0.02 and 2.4%, respectively, in total neutral extract, RPK type), and the other having phyllocladene (55%) accompanied with a small amount of rimuene and 1 (0.1 and 1.2%, RP type) were crossed by use of pollen of a C. japonica (Sugi) having ent-kaurene (34%, K type). The diterpene type and its distribution of the hybrids are shown in Table 1. One R type from RPK x K and one RP type from RP x K were used for bulk extraction and chromatographic separation. ent-Rosa-5,15-diene (1) and a small amount of ent-sclarene was obtained from the former, and phyllocladene and 1 from the latter.

Thus, the mother trees contained both 1 and rimuene, the latter was limited to accompanying phyllocladene, but the former could appear as the main diterpene. In spite of extensive research of Yasue et al. [5] (more than 5000 trees were analysed), 1 was not found in C. japonica. Therefore, the presence of 1 seems to be a distinguishing feature of C. fortunei from C. japonica. The P-type of both species was examined in detail. A total of 12 P-type C. japonica (four wild trees from central Kyushu mountains, two cultivars and six wild from Yakushima) had no sign of presence of 1, although 10 of which contained 0.02-0.1% rimuene to phyllocladene. On the other hand, all four P-types of C. fortunei (which had no kaurene) contained 0.3-2.2% of 1 besides a trace of rimuene.

A RS type of Sugi, which was not reported previously, was found in C. japonica of Yakushima and the components were identified as 1 and ent-sclarene. The RK type, which may get confused with 'KS type' in the report of Yasue [5] as one of the characteristics on 'Yaku-Sugi', was also found. Thus, the population containing 1 in Yakushima may be expected to be considerable and it is an important factor for follow-up work on Cryptomeria species.

EXPERIMENTAL

Optical rotation was measured in 1% CHCl₃ soln unless specially mentioned. The NMR spectra were measured in CDCl₃. GC was carried out using a capillary column of PEG 20M 25 m. Analysis of 1 and rimuene was carried out at 190°. Extraction of leaves and analysis were as described in a previous report [8].

Separation. Leaves of a hybrid of R type (GC analysis; 1 30; S, 3%; 427 g) were extracted with hexane for 4 days. The neutral extract (3.18 g) was chromatographed on alumina (102 g). The eluates were distilled before the measurement of optical rotation. Compound 1 (346 mg) from a hexane eluate had [α]D₂₀ = -41.0°. 13CNMR was identical with lit [6]. The 2nd fr was ent-sclarene (19 mg), [α]D₂₀ = -32.0°. Similar treatment of a hybrid of RP type
Table 1. Leaf oil diterpene type of hybrids from C. fortunei and C. japonica

<table>
<thead>
<tr>
<th>Hybrid diterpene type</th>
<th>Motile</th>
<th>Ratio</th>
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<tr>
<td></td>
<td>RPK</td>
<td>RP</td>
</tr>
<tr>
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<td>3</td>
</tr>
<tr>
<td>RPK</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>RPk</td>
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<td>1</td>
</tr>
</tbody>
</table>

K; ent-kaurene, R; ent-rosa-5,15-diene, P; phyllocladene, S; (ent-)sclarene, Ri; rimuene.

(GC analysis; I, 14; P, 19; S, 0.3%; 443 g) afforded 2.50 g of neutral extract from which a hydrocarbon fraction (46/ mg) was obtained. It was subjected to a AgNO₃ impregnated silica gel column, and phyllocladene containing 5% of sandaracopimaradiene isomer [5] (221 mg), [α]D + 13.3° and I (138 mg) [α]D − 40.8° were obtained. Phyllocladene was purified through vacuum sublimation, mp 99°.

One C. japonica specimen from Yakushima showed the diterpene type of RS (GC analysis 1, 19; S, 13% and 6 other minor diterpene peaks, but no rimuene). A bulk extraction of 700 g of leaves gave 2.71 g of neutral extract. Chromatographic sepn with an alumina column (100 g) and distillation of the eluate gave I (127 mg) [α]D − 44.6° and ent-sclarene (89 mg) [α]D − 32.5°.

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REFERENCES