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# The Sesquiterpenes of *Dendropanax trifidus*

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**Synopsis.** The volatile oils of the leaves, cortex and fruits of *Dendropanax trifidus* were investigated. Germacrene-D is enantiomeric, sesquiterpenes of other series, such as caryophyllene and selinenes, optically corresponding to those in higher plants.

Some volatile oils of *Aralia* species have simple compositions, consisting of germacrene-D, caryophyllene, humulene, *etc.*[1] We have studied the volatile oils of *Dendropanax trifidus*.

The volatile oils of the leaves, cortex and fruits were obtained by steam distillation, the components being isolated by silica gel column and gas chromatography. The isolated compounds and their $[\alpha]_D$ values are given in Table 1. Caryophyllene (**1**) was the major component in the leaf oil, the series, α- and β-neoclovenes(**2** and **3**) and β-panasinsene (**4**) being detected. The occurrence of **4** in nature is significant since it has been suggested to be a key intermediate in the caryophyllene-neoclovene conversion reaction.[2] Cadalene-type compounds (**6**—**9**) and selinenes (**10** and **11**) were also detected. In contrast to the leaf oil, only a trace of caryophyllene was found in the cortex oil, germacrene-D (**5**), a potential precursor of cadalene-type compounds, bourbonenes, *etc.*,[3] being the major component. These serial compounds were also detected. Selinenes were found in small amounts. In the fruit oil, almost all caryophyllene disappeared and no germacrene-D was present. However, various derivatives such as cadinenes (**6** and **7**) and muurolenes (**8** and **9**) were found together with neoclovenes and selinenes. A large amount of humulene was found in this oil. It is probable that caryophyllene and germacrene-D were further transformed into compounds, **2**, **3** and **6**—**9** for final storage in the fruits.

It is noteworthy that germacrene-D in the plant is dextrorotatory, containing an α-isopropyl group as shown in Fig. 1. The optical rotations show that the compounds of the germacrene-D series have also α-isopropyl groups, being enantiomers of those occurring in higher plants.[3] On the other hand, the selinenes have β-isopropyl groups. Thus, in this plant, germacrene-D series compounds and selinenes, which may be derived from a common germacrene-type precursor (**12**), have enantiomeric isopropyl configurations.

Table 1. Compounds isolated from *D. trifidus*

| Compounds | Leaf oil (%) | Cortical oil (%) | Fruit oil (%) | $[\alpha]_D$ (°) |
|---|---|---|---|---|
| Caryophyllene series | | | | |
| caryophyllene (**1**) | 63 | trace | trace | −14 |
| α-neoclovene (**2**) | 2 | — | 4 | −50 |
| β-neoclovene (**3**) | 3 | — | 6 | −30 |
| β-panasinsene (**4**) | 2 | trace | trace | |
| isocaryophyllene | 2 | — | — | |
| caryophyllene oxide | 1 | — | — | |
| Germacrene-D series | | | | |
| germacrene-D (**5**) | — | 73 | — | +305 |
| γ-cadinene (**6**) | 3 | 6 | 8 | −62 |
| δ-cadinene (**7**) | 2 | 3 | 23 | −53 |
| α-muurolene (**8**) | 1.5 | 2 | 1 | +58 |
| γ-muurolene (**9**) | 5 | 7 | 3 | −2 |
| β-bourbonene | trace | — | — | |
| β-copaene | trace | — | — | |
| calamenene | — | 1 | — | |
| Selinene series | | | | |
| α-selinene (**10**) | 2 | trace | 3 | +68 |
| β-selinene (**11**) | 3 | 1.5 | 7 | +49 |
| Others | | | | |
| δ-elememe | trace | — | — | |
| β-farnesene | 1.5 | — | 2 | |
| α-humulene | 2 | — | 32 | |

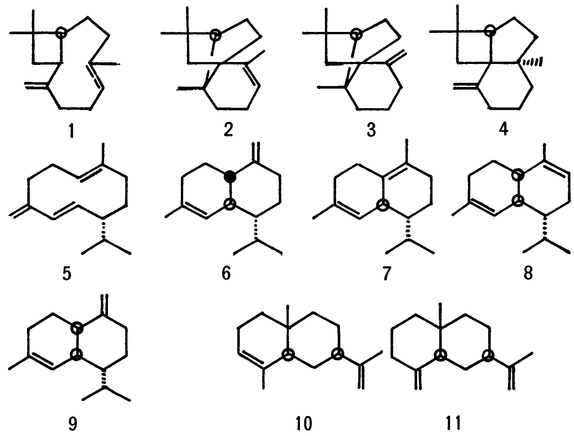


Fig. 1. Structures of selected compounds from Table 1.

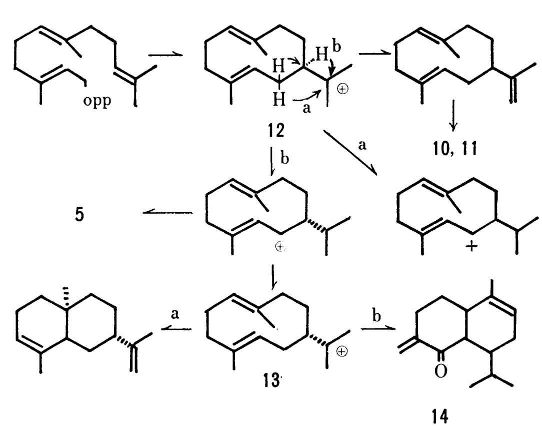


Fig. 2. Possible biosynthetic route involving enantiomeric germacrenoidal precursors (see the text).

Such coexistence of enantiomeric germacrene-D series and normal selinene-type compounds in a higher plant does not seem to have been found. A similar case was reported for a sort of liverwort, *Chiloscyphus polyanthus*, in which, in contrast to *D. trifidus*, $\alpha$-selinene has an $\alpha$-isopropyl group, and chiloscyphone (**14**), a cadalene-type ketone, has a $\beta$-isopropyl group.[4] Andersen *et al.* suggested that $\alpha$-selinene and chiloscyphone in *C. polyanthus* are derived from enantiomeric germacrenoidal precursors (**12** and **13**, respectively). However, an alternative biogenetic route is also possible, *i.e.*, a single 1,3-hydride shift (path a) and two concerted 1,2-hydride shifts (path b) in the germacrenium-cation (**12**) can occur, resulting in an opposite orientation of the isopropyl group. If this is the case, the unusual coexistence of chiloscyphone with other enantiomeric compounds in *C. polyanthus* can be explained by the inversion of its isopropyl group through path b. Thus, *C. polyanthus* resembles other liverworts producing enantiomeric terpenes. The coexistence of enantiomeric germacrene-D series compounds in *D. trifidus* appears to support this view.

## Experimental

*Analytical Instrument.* Analytical gas chromatography was carried out on a Hitachi-063-type apparatus fitted with a HB-2000 capillary column. Measurements of physical data were taken on a Hitachi EPI-G-2-type IR absorption spectrometer with NaCl cell, a JEOL-JNM-C-60-type NMR spectrometer and a Perkin-Elmer's 141-type polarimeter.

*Isolation.* The materials were collected in Osaka prefecture. 5.2 g of leaf oil (from 25 kg, 0.02%), 2.7 g of the cortical oil (from 12 kg, 0.02%), and 11.7 g of the fruit oil (from 8 kg, 0.146%) were obtained by steam distillation. Each oil was chromatographed on silica gel using hexane–ether as the carrier. Each eluted fraction was separated into pure compounds by means of a Varian MODEL-90-P-type gas chromatograph fitted with a Carbowax 20 M column.

## References

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