Isolation of Agarofuran-type Sesquiterpenes from 
*Alpinia japonica* (Thunb.) Miq. 1)

A new sesquiterpene, 3α,4α-oxidoagarofuran (2) was isolated besides 4-hydroxy-
dihydroagarofuran (1), 3α-agarofuran (3) and β-eudesmol (4) from the rhizomes of *Alpinia japonica*.

Biogenetically, it is interesting that β-eudesmol is isolated from same plant together 
with agarofurans, which possess 10-epimeric eudesmane carbon skeleton.

**Keywords**—Zingiberaceae; *Alpinia japonica* (Thunb.) Miq.; sesquiterpene; 4α-
hydroxydihydroagarofuran; 3α,4α-oxidoagarofuran; α-agarofuran; β-eudesmol; 10-epi-
eudesmane-type

The seeds of *Alpinia japonica* (Thunb.) Miq. (Zingiberaceae) are used as an aromatic 
stomachic under the name, “Izu-shukusha” (伊豆縮砂), in Japan.

Several flavonoids (alpinon, izalpinin, kumatkenin and rhammocitrin) and monoterpenes 
(camphor and cineole) have been isolated from the seeds by Kimura and co-workers. 2) They 
have also reported the presence of sesquiterpene alcohols in the essential oil of the seeds, but 
little has been known about their structures. 3)

In this paper, we wish to report the isolation and characterization of four sesquiterpenes 
including a new compound from the rhizomes of this plant.

The fresh rhizomes were extracted with methanol, and the aqueous methanolic extracts 
were partitioned with petroleum ether. The petroleum ether soluble fraction was repeatedly 
separated and purified by silica gel and silver nitrate impregnated silica gel chromatography 
to give four compounds (1—4).

Compound (1), C_{15}H_{26}O_{2}, colorless needles, mp 128.5—129.5°, showed a strong hydroxyl 
absorption band at 3430 cm⁻¹ in the IR spectrum. The ¹H-NMR spectrum (CDCl₃) revealed 
four tertiary methyl signals (δ 1.17, 1.21, 1.27, 1.36), and the ¹³C-NMR spectrum (CDCl₃) 
indicated the presence of ether linkage [δ 82.1 (s), 87.8 (s)]. Taking account of its molecular 
formula, we assumed from above facts that compound (1) might be 4α-hydroxydihydroagarofu-

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furan, which has already been isolated from fungus infected agarwood (*Aquilaria agallocha* Roxb.). However, because the authentic sample was not available and this is a key compound for the structure elucidation of the following compounds (2 and 3), the structure of 1 was unequivocally determined by X-ray analysis.4)

Compound (2) was obtained as colorless oil, $[\alpha]_D^{22} = -20.8^\circ$ (c=0.39, EtOH); molecular formula, $C_{16}H_{22}O_3$ was confirmed by high resolution mass spectrum, $m/e$ 236.1764 (M⁺, Calcd for $C_{16}H_{22}O_3$: 236.1776); IR (liquid film) 2920, 1390, 1155, 1145, 1010, 970, 895 cm⁻¹, no hydroxyl absorption; $^1$H-NMR (CDCl₃) 1.13, 1.25, 1.31, 1.37 (3H, each, s), 3.00 (1H, broad d, $\text{O} \quad \text{C} \quad \text{C} \quad \text{H}$); $^{13}$C-NMR (CDCl₃) 18.6 (q), 20.7 (t), 22.7 (q x 2), 24.3 (t), 30.0 (q), 31.8 (t), 32.1 (t), 36.9 (t), 37.5 (s), 44.3 (d), 59.9, 60.7 (s and d, $\text{O} \quad \text{C} \quad \text{C} \quad \text{H}$), 82.3 (s), 85.0 (s).

The above spectral evidences suggested that this compound might be an epoxide of $\alpha$-agarofuran. Reductive cleavage of the epoxide (2) with lithium aluminum hydride gave colorless needles, which was identical with compound (1). Consequently, the compound (2) can be formulated as 3x,4x-oxidoagarofuran.

![Chart 1](chart1.png)

Compound (3), $C_{15}H_{24}O$, oily, was identified as $\alpha$-agarofuran by comparison of the spectral data with those reported.3)

Compound (4), $C_{15}H_{26}O$, colorless needles, mp 80.5—81.5°, was also identified as $\beta$-eudesmol by comparison with an authentic sample including specific rotation.

Agarofurans (1—3) possess the 10-epieudesmane skeleton, and could be supposed to form biosynthetically from hedycaryol in the conformation in which the methyl group are mutually *syn* but *anti* with respect to the $-\text{(CH}_3)_{10}\text{OH}$ grouping.5) $\beta$-Eudesmol (4) could also be derived from the same precursor through another conformation. Therefore, it is noteworthy that we found these two types of sesquiterpene in the same plant. Only a few similar instances have been reported recently.5,6)

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4) Detail data will be reported later.