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Studies on the Constituents of the Plants of *Illicium* Species. III.[1] Structure Elucidations of Novel Phytoquinoids, Illicinones and Illifunones from *Illicium tashiroi* MAXIM. and *I. arborescens* HAYATA

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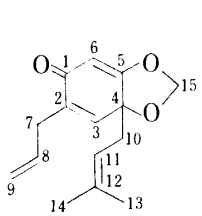
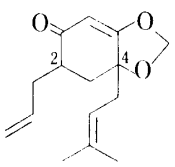
Chemical constituents of the leaves of *Illicium tashiroi* and *I. arborescens* (Illiciaceae) were examined. Novel phytoquinoids, (+)-illicinone-A (**1a**), -B (**2a**), -C (**3a**), and -D (**4a**), and illifunone-A (**5a**) and -B (**5b**) were isolated from *I. tashiroi*, and characterized. As constituents of *I. arborescens*, enantiomers (**1b** and **2b**) of (+)-illicinone-A (**1a**) and -B (**2a**), and diastereoisomers (**2c**, **3b**, **4b**, and **4c**) of (+)-illicinone-B (**2a**), -C (**3a**), and -D (**4a**) were characterized. The absolute stereochemistry of (−)-illicinone-A was established by analysis of the circular dichroism (CD) spectra of the α-hydroxy ketones (**15** and **16**) derived from **1b**. The stereochemistries of other illicinones and illifunones deduced from the chemical and/or biogenetic correlations.

Keywords——*Illicium tashiroi*; *Illicium arborescens*; Illiciaceae; illicinone; illifunone; phytoquinoid; hydroxycyclohexanone; CD; ^{1}H-NMR; ^{13}C-NMR

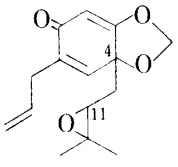
Phytoquinoids, of which only a few examples are known to occur in higher plants, are of interest because of their antitumor and cytotoxic activities.[2-4] In a preliminary communication,[5] we described the isolation of novel phytoquinoids, (+)-illicinone-A, -B, -C, and -D, from leaves of *Illicium tashiroi* MAXIM. (Japanese name, *Yaeyama-shikimi*) (Illiciaceae) collected on Iriomote island, and the plane structures **1a**, **2a**, **3a**, and **4a** were proposed, respectively.



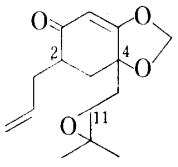
1a[a]: 4*S*
1b[b]: 4*R*



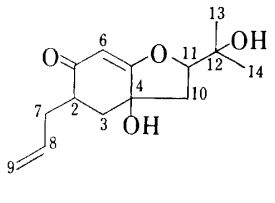
2a[a]: 2*R*, 4*S*
2b[b]: 2*S*, 4*R*
2c[b]: 2*R*, 4*R*



3a[a]: 4*S*, 11*S*
3b[b]: 4*R*, 11*S*
3c : 4*S*, 11*R*
3d : 4*R*, 11*R*



4a[a]: 2*R*, 4*R*, 11*S*
4b[b]: 2*S*, 4*S*, 11*S*
4c[b]: 2*R*, 4*S*, 11*S*
4d : 2*R*, 4*R*, 11*R*
4e : 2*R*, 4*S*, 11*R*



5a[a]: 2*S*, 4*R*, 11*R*
5b[a]: 2*R*, 4*R*, 11*R*
5c[b]: 2*R*, 4*S*, 11*R*
5d[b]: 2*S*, 4*S*, 11*R*

[a] Components of *I. tashiroi*
[b] Components of *I. arborescens*

Chart 1

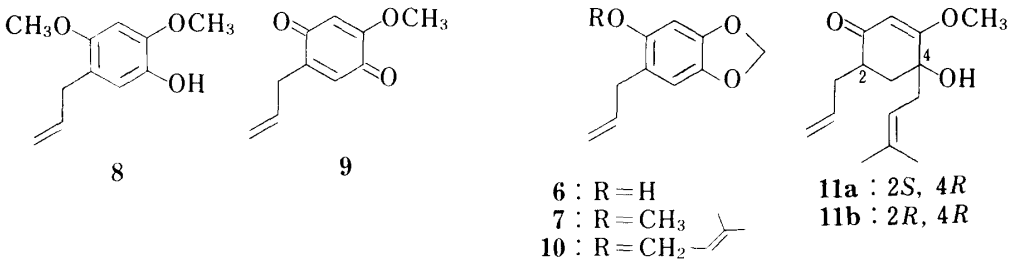
In the course of these studies, we also examined the components of leaves of *I. arborescens* HAY. (Japanese name, *Akabana-shikimi*) collected in Taiwan. Interestingly, we found that enantiomers (**1b** and **2b**) of (+)-illicinone-A (**1a**) and -B (**2a**), and diastereoisomers (**2c**, **3b**, **4b**, and **4c**) of (+)-illicinone-B (**2a**), -C (**3a**), and -D (**4a**) were present in *I. arborescens*, and new cyclic phytoquinoids, illifunone-A (**5a**) and -B (**5b**) from *I. tashiroi*, and illifunone-C (**5c**) and -D (**5d**) from *I. arborescens* were also found and characterized.

This paper gives full details of structure elucidations of the illicinones (**1**—**4**) and illifunones (**5**) obtained from *I. tashiroi* or *I. arborescens*.[6]

Results and Discussion

The Structure of Illicinone-A (1)

(+)-Illicinone-A was obtained as a colorless oil, $[\alpha]_D$ +95° (in chloroform). The ultraviolet (UV) and infrared (IR) spectra showed absorptions typical of a 3-oxygenated 2,5-cyclohexadien-1-one system[4] [λ_{max} 237, and 283 nm; ν_{max} 1665, 1630, and 1610 cm^{-1}]. In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table I), a lower field one-proton singlet at δ 6.54 having a long-range coupling was assigned to a proton attached to the β-carbon in the α,β-unsaturated carbonyl moiety. Three one-proton sharp singlets at δ 5.47, 5.54, and 5.56, in view of the presence of a triplet at δ 97.9 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table III), were assignable to two protons of a methylenedioxy group and an olefinic proton attached to the α-carbon of the α,β-unsaturated carbonyl system. However, accurate assignment was difficult.[7] The presence of a prenyl and an allyl moiety was indicated by the ^{1}H- and ^{13}C-NMR signals as follows: prenyl, δ_H 1.54 (3H, s), 1.68 (3H, s), 2.43 (2H, br d, J=7 Hz), 4.95 (1H, m); δ_C 17.8 (q), 25.7 (q), 34.7 (t), 115.8 (d), 137.1 (s). Allyl, δ_H 3.01 (2H, d, J=7 Hz), 4.95 (1H, m) 5.10 (1H, br s), 5.78 (1H, m); δ_C 33.3 (t), 116.8 (t), 134.6 (d). The observation of the fragment peak at m/z 178 as the base peak due to a prenyl radical lost from the molecular ion at m/z 246 with a hydrogen transfer in the mass spectrum was suggestive of the location of the prenyl group at the allylic carbon, C-4.



8 9

6 : R=H
7 : R=CH_3
10 : R=CH_2—

11a : 2*S*, 4*R*
11b : 2*R*, 4*R*

Chart 2

Treatment of (+)-illicinone-A with 5% hydrochloric acid in methanol at room temperature gave four oily products from which a prenyl group had been eliminated; they were characterized on the basis of IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS) as structures **6**, **7**, **8**, and **9**. Treatment of **6** with prenyl bromide in the presence of sodium hydride in dimethyl formamide gave an oil in 3% yield along with **10** as the major product (65% yield).[1] The IR and ^{1}H-NMR spectra of this oil were superimposable on those of (+)-illicinone-A obtained from natural sources. On the basis of these results, the plane structure of (+)-illicinone-A should be represented by the formula **1**.

The elucidation of the absolute configuration at C-4 in (+)-illicinone -A (**1a**) was carried out by using the enantiomer of (+)-illicinone-A, because the (−)-isomer was easily obtained from *I. arborescens*. Sodium borohydride reduction of (−)-illicinone-A (**1b**) in methanol

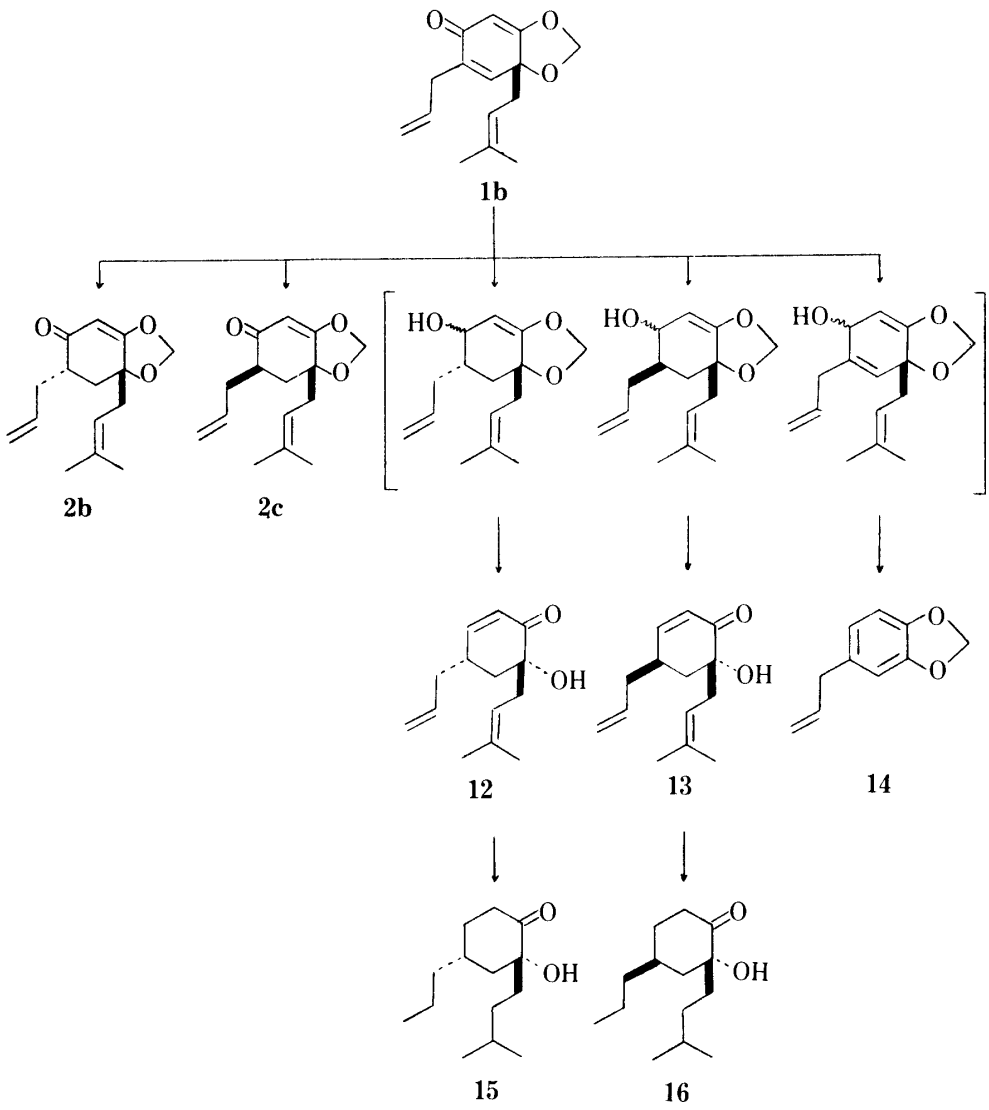


Chart 3

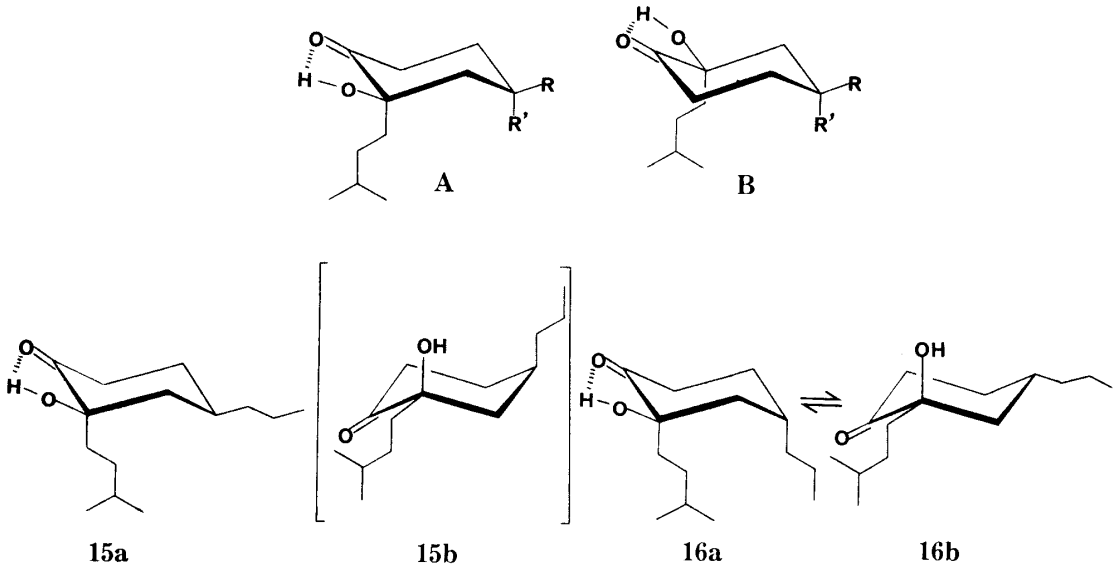


Chart 4

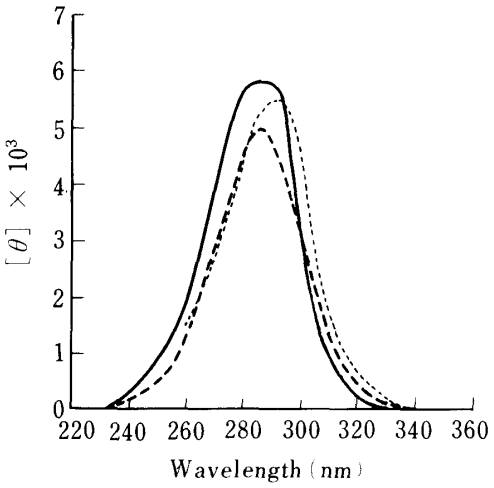


Fig. 1. Circular Dichroism Curves of (+)-2-Hydroxycyclohexanone (**15**)

——, in isooctane; ------, in $(CH_3)_2SO$; - - - -, in CH_3OH.

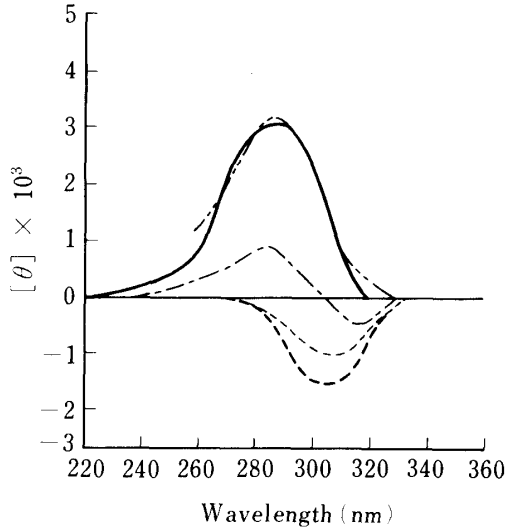


Fig. 2. Circular Dichorism Curves of (+)-2-Hydroxycyclohexanone (**16**)

——, in isooctane; - - - -, in CCl_4; - - - -, in CH_3CN; ------, in $(CH_3)_2SO$; - - - -, in CH_3OH.

afforded 2-hydroxycyclohexenones **12** and **13**, and safrole (**14**) along with **2b** and **2c** corresponding to conjugated reduction products of the starting material. Among them, compound **2b** was indicated to be an enantiomer of (+)-illicinone-B (**2a**) isolated from *I. tashiroi* by comparisons of IR, ^{1}H-NMR, MS, and optical rotation. Compounds **12** and **13** were considered to be derived from the corresponding tetrahydro intermediates by an acid-catalyzed allylic rearrangement, as shown in Chart 3. Compounds **2b** and **2c** also gave **12** and **13**, respectively, on treatment with sodium borohydride followed by acid. Catalytic hydrogenation of **12** and **13** afforded the 2-hydroxycyclohexanones **15** and **16**, respectively.

The conformation analysis of α-hydroxy cyclic ketones has been investigated in detail by Suga *et al.*[8,9] We applied their methods to elucidate the stereochemistry of illicinone-A (**1**).

The IR spectra of **15** and **16** in carbon tetrachloride showed concentration-independent bands at 3480 and 3475 cm^{-1}, respectively, owing to an intramolecular hydrogen bonded hydroxyl function. Thus, two chair conformations of each compound are possible, A and B (R=propyl, R′=H, and *vice versa*, Chart 4), considering the difference of absolute configuration. The circular dichroism (CD) spectra of both **15** and **16** (Figs. 1 and 2) derived from (−)-illicinone-A exhibited a positive Cotton effect in a nonpolar solvent (isooctane). Therefore, **15** and **16** were established to have the structure A (R=propyl, R′=H, and *vice versa*) in Chart 4. The CD spectrum of **15** still showed only a positive Cotton effect in polar solvents, whereas inversion of the sign of the Cotton effect in the CD spectrum of **16** was observed upon changing the polarity of the solvent (Fig. 2).

On the basis of these results, the absolute configuration of the carbon carrying the hydroxy group could be established to be *R*. Further, **15** was considerd to exist predominantly in conformation **15a** in both nonpolar and polar solvents, while **16** adopts the conformer **16a** preferentially in a nonpolar solvent, and there is an equilibrium between **16a** and **16b** in polar solvents. Finally, the absolute configuration of (−)-illicinone-A obtained from *I. arborescens* was established to be 4*R*, and that of (+)-illicinone-A isolated from *I. tashiroi* was assigned as 4*S*, as shown in formulae **1b**, and **1a**, respectively.

The Structure of Illicinone-C (3)

(+)-Illicinone-C was obtained as a colorless oil, $[\alpha]_D$ +128° (in chloroform). The

similarities of the IR (ν_{max} cm^{-1}: 1677, 1640, 1618) and the UV spectra with those of 4*S*-(+)-illicinone-A (**1a**) were suggestive of the presence of the 2,5-cyclohexadien-1-one nucleus in (+)-illicinone-C as in **1a**. The ^{1}H-NMR spectrum of (+)-illicinone-C exhibited, instead of the olefinic and methylene proton signals due to the prenyl moiety as seen in **1a**, new ABC type signals at δ 1.73 (dd, J=8, 15 Hz), 2.24 (dd, J=5, 15 Hz), and 2.80 (dd, J=5, 8 Hz). Other ^{1}H-NMR signals as shown in Table I were nearly identical in form and multiplicity with the signals for the corresponding groups of **1a**. Furthermore, in a comparison of the ^{13}C-NMR spectra of **1a** and (+)-illicinone-C, a doublet at δ 115.8 and a singlet at δ 137.1 in **1a** were observed to be shifted upfield at δ 58.9 (d), and 58.1 (s), respectively in (+)-illicinone-C. These data showed the presence of an epoxidized prenyl moiety in the molecule of (+)-illicinone-C, instead of the prenyl group in **1a**. Treatment of **1a** with *m*-chloroperbenzoic acid in dichloromethane afforded two products. One of them was shown to be identical with (+)-illicinone-C by comparisons of IR, ^{1}H-NMR, MS, and optical rotation. The other product was considered to be an epimer at the epoxidized carbon at C-11. Epoxidation of (−)-illicinone-A (**1b**) with *m*-chloroperbenzoic acid afforded **3b** and **3d**. Compound **3b** was also obtained from *I. arborescens*. From these spectral and chemical results, the structure of (+)- and (−)-illicinone-C could be assigned as **3a**, and **3b**, respectively, except for the configuration at C-11.

The Structure of Illicinone-B (2)

(+)-Illicinone-B was isolated as a colorless oil, $[\alpha]_D$ +140° (in chloroform). The UV and IR spectra showed absorption bands at λ_{max} 249 nm, and ν_{max} 1630 cm^{-1}, respectively. The appearance of unresolved overlapping multiplets in the range from 2.2 to 2.8 ppm in the ^{1}H-NMR spectrum and a triplet at δ 30.4 and a doublet at δ 42.0 in the ^{13}C-NMR spectrum, instead of a characteristic low field signal at δ 6.54 due to an olefinic proton at the β-carbon of the α,β-unsaturated carbonyl system, and a doublet at δ 134.1 and a singlet at δ 139.0 due to C-3 and C-2 in **1a**, respectively, led to the structure of (+)-illicinone-B shown by **2**, corresponding to the 2,3-dihydro derivative of illicinone-A (**1**). As already mentioned above, the enantiomer (**2b**) of 4*S*-(+)-illicinone-B (**2a**) was isolated from *I. arborescens* along with its diastereoisomer (**2c**), and was also obtained by the treatment of 4*R*-(−)-illicinone-A (**1b**) with sodium borohydride in methanol along with **2c**. Treatment of 4*R*-(−)-illicinone-B (**2b**) with sodium methoxide afforded methoxycyclohexene **11a** as a sole product. On the other hand, similar treatment of the 2-epimer (**2c**) of 4*R*-(−)-illicinone-B (**2b**) gave 4*R*-(−)-illicinone-B (**2b**), **11a**, and **11b**.[10] Consequently, the allyl group attached at C-2 in 4*R*-(−)-illicinone-B (**2b**) was in a stable form when compared with that of its epimer **2c**. From these results, the structures of (+)-illicinone-B, (−)-illicinone-B, and its C-2 epimer should be represented by the formulae **2a**, **2b**, and **2c**, respectively.

The Structure of Illicinone-D (4)

(+)-Illicinone-D, a colorless oil, $[\alpha]_D$ +171° (in chloroform), showed ^{1}H- and ^{13}C-NMR signals very similar to those of **2a**, except for the signals of the prenyl moiety, as shown in Tables I and III. The new signals at δ 1.56 (dd, J=9, 15 Hz), 2.28 (dd, J=3, 15 Hz), and 2.93 (dd, J=3, 9 Hz) could be assigned to ABC type signals of H-10 and H-11. Furthermore, in the ^{13}C-NMR spectrum of (+)-illicinone-D, a singlet at δ 57.1 and a doublet at δ 59.1 were observed instead of the signals at δ 136.2 (s) and 116.5 (d) in the spectrum of **2a**. These relationships between the spectral data of **2a** and (+)-illicinone-D were the same as in the case of **1a** and **3a**. Epoxidation of 4*S*-(+)-illicinone-B (**2a**) with *m*-chloroperbenzoic acid gave (+)-illicinone-D as one of the reaction products. Another reaction product was shown to be an enantiomer (**4d**) of **4b** isolated from *I. arborescens* by comparisons of IR, and ^{1}H-NMR spectra and optical rotation. On the basis of these results, (+)-, and (−)-illicinone-D can be represented by the formulae **4a**, and **4b**, respectively, except for the configuration at C-11.

Further (−)-illicinone-D (**4c**) was also isolated from *I. arborescens*, and its structure was confirmed by comparison with one of the epoxidized products of **2c**.

The Structure of Illifunone-A (5a)

Illifunone-A forms colorless needles from chloroform, mp 107—110 °C, $[\alpha]_D$ −202° (in chloroform). The IR spectrum showed characteristic bands at 3590, 3360, and 1638 cm^{-1} attributable to hydroxyl groups and α,β-unsaturated carbonyl group, respectively. The absorption at 257 nm in the UV spectrum indicated the presence of an α,β-unsaturated carbonyl moiety carrying *O*- and *C*-substituents at the β-carbon. Acetylation of illifunone-A with acetic anhydride in pyridine at room temperature or methylation with diazomethane did not occur, indicating the presence of tertiary hydroxyl groups. The ^{1}H-NMR spectrum (Table II) showed the vinyl proton signals of an allyl group as multiplets at δ 5.71 and 5.02, the α-proton of the α,β-unsaturated carbonyl moiety as a singlet at δ 5.33, and two methyl singlets at δ 1.50 and 1.28. Furthermore, a ABC type signal assigned to H-10 and H-11 was observed at δ 4.42 (J=2, 9 Hz), 2.40 (J=2, 14 Hz), and 2.17 (J=9 and 14 Hz) as double doublets. A comparison of the ^{13}C-NMR spectra (Table III) of illifunone-A and 2*R*,4*S*-(+)-illicinone-B (**2a**) showed that a doublet at δ 116.5 and a singlet at δ 136.2 in **2a** were shifted upfield to δ 90.5 (d) and 71.4 (s), respectively, in illifunone-A, and a methylenedioxy carbon triplet at δ 97.3 in **2a** was absent in illifunone-A. Other ^{13}C-NMR signals of illifunone-A are nearly identical with those of **2a**. The configuration of the allyl group at C-2 could be assigned as equatorial since an axial–axial coupling (J=12 Hz) was seen at H-3 (δ 1.63) in the ^{1}H-NMR spectrum. The stereochemistry of C-4 was presumed on biogenetic grounds to be the same as that in (+)-illicinones (**1a**—**4a**) existing in the same plant, although this was not directly proved.

Consideration of these results led to the structure **5a** for illifunone-A, excluding the stereochemistry at C-11.

The Structure of Illifunone-B (5b)

Illifunone-B forms colorless needles from chloroform, mp 149—151 °C, $[\alpha]_D$ −177° (in chloroform). The IR, UV, and MS were almost identical with these of **5a**. The ^{1}H-NMR spectrum of illifunone-B also exhibited signals of vinyl protons (δ 5.72 and 5.07) of an allyl group, the α-proton (δ 5.36) of an α,β-unsaturated carbonyl system, and ABC type signals of H-10 and H-11 [δ4.43 (J=2, 8 Hz), 2.43 (J=2, 11 Hz), and 2.14 (J=8, 11 Hz)], being similar to those of **5a**. However, in the ^{1}H-NMR spectrum of illifunone-B, only an axial–equatorial coupling was observed at axial H-3 (δ 1.85, dd, J=4, 11 Hz), instead of axial–axial coupling at H-3 (δ 1.63, t, J=12 Hz) as seen in **5a**. These spectral data coupled with the ^{13}C-NMR spectrum (Table III), suggested the structure of illifunone-B to be **5b**, corresponding to the C-

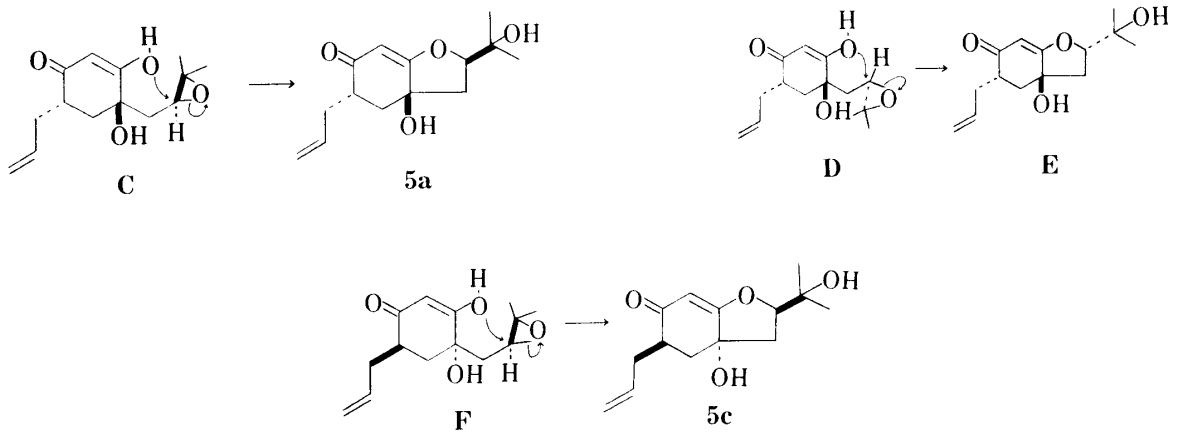


Chart 5

TABLE I. ^{1}H-NMR Spectral Data for Illicinones

Proton No.	**1a, b**	**2a, b**	**2c**	**3a**	**3b**	**4a**	**4b**	**4c**
H-2 (1H)	—	a)	a)	—	—	a)	a)	a)
H-3 (1H)	6.54 (s)[b]	a)	a)	6.79 (s)[b]	6.71 (s)	a)	a)	a)
H-6 (1H)	5.47 (s)[d]	5.35 (s)[d]	5.42 (s)[d]	5.55 (s)[d]	5.56 (s)[d]	5.36 (s)[d]	5.40 (s)[d]	5.42 (s)[d]
H-7 (2H)	3.01 (d, $J=7$)[b]	a)	a)	3.07 (d, $J=7$)[b]	3.08 (d, $J=7$)	a)	a)	a)
H-8 (1H)	5.78 (m)	5.66 (m)	5.70 (m)	5.84 (m)	5.79 (m)	5.72 (m)	5.68 (m)	5.70 (m)
H-9 (2H)	5.10 (br s)	5.06 (m)	5.14 (br s)	5.15 (br s)	5.17 (br s)	5.10 (m)	5.12 (m)	5.14 (m)
	4.95 (m)	4.95 (m)	5.00 (m)	5.02 (m)	5.04 (m)	4.96 (m)	5.04 (m)	5.00 (m)
H-10 (2H)	2.43 (br d, $J=7$)	a)	a)	1.73 (dd, $J=8$, 15)	1.81 (dd, $J=6$, 14)	1.56 (dd, $J=9$, 15)	a)	a)
				2.24 (dd, $J=5$, 15)	2.22 (dd, $J=6$, 14)	2.28 (dd, $J=3$, 15)		
H-11 (1H)	4.95 (m)	5.13 (m)	5.22 (m)	2.80 (dd, $J=5$, 8)	2.71 (t, $J=6$)	2.93 (dd, $J=3$, 9)	2.88 (t, $J=5$)	2.94 (dd, $J=4$, 7)
H-13 (3H)	1.54 (s)[c]	1.64 (s)[c]	1.65 (s)[c]	1.23 (s)[c]	1.20 (s)[d]	1.28 (s)[c]	1.28 (s)[c]	1.29 (s)[c]
H-14 (3H)	1.68 (s)[c]	1.76 (s)[c]	1.78 (s)[c]	1.30 (s)[c]	1.28 (s)[d]	1.36 (s)[c]	1.35 (s)[c]	1.36 (s)[c]
H-15 (2H)	5.54 (s)[d]	5.43 (s)[d]	5.42 (s)[d]	5.55 (s)[d]	5.56 (s)[c]	5.49 (s)[d]	5.51 (s)[d]	5.46 (s)[d]
	5.56 (s)[d]	5.49 (s)[d]	5.54 (s)[d]	5.63 (s)[d]	5.63 (s)[c]	5.58 (s)[d]	5.56 (s)[d]	5.55 (s)[d]

a) These signals could not be assigned because they overlapped with other signals (**2a**, **b**, 2.15—2.76 ppm; **2c**, 1.87—2.89 ppm; **4a**, 2.20—2.80 ppm; **4b**, 1.87—2.75 ppm; **4c**, 1.94—2.80 ppm).
b) Long-range coupling was observed.
Figures in parentheses are coupling constants in Hertz.
c, d) Assignments with the same superscript (*c* and *d*) in the same column could be interchanged.

Table II. ^{1}H-NMR Spectral Data for Illifunones

Proton No.	5a	5b	5c	5d
H-3 (1H)	1.63 (t, J=12)	1.85 (dd, J=4, 11)	1.71 (t, J=12)	1.89 (dd, J=4, 11)
H-6 (1H)	5.33 (s)	5.36 (s)	5.27 (s)	5.38 (s)
H-8 (1H)	5.71 (m)	5.72 (m)	5.86 (m)	5.80 (m)
H-9 (2H)	5.08 (m)	5.16 (m)	5.06 (m)	5.19 (m)
	4.94 (m)	5.01 (m)	4.92 (m)	5.04 (m)
H-10 (2H)	2.17 (dd, J=9, 14)	2.14 (dd, J=8, 11)	1.95 (dd, J=10, 13)	
	2.40 (dd, J=2, 14)	2.43 (dd, J=2, 11)	2.36 (dd, J=5, 13)	
H-11 (1H)	4.42 (dd, J=2, 9)	4.43 (dd, J=2, 8)	4.68 (dd, J=5, 10)	4.66
H-13 (3H)	1.28 (s)[a]	1.29 (s)[a]	1.17 (s)[a]	1.18 (s)[a]
H-14 (3H)	1.50 (s)[a]	1.52 (s)[a]	1.37 (s)[a]	1.39 (s)[a]

H-2 (1H), H-3 equatorial (1H), and H-7 (2H) could not be assigned because of mutual overlapping (**5a**, 2.97—2.00 ppm, **5b**, 2.76—2.35 ppm, **5c**, 2.95—2.00 ppm, **5d**, 2.70—2.07 ppm).
Figures in parentheses are coupling constants in Hertz.
a) Assignments with the superscript *a*) in the same column could be interchanged.

2 isomer of illifunone-A (**5a**).

The Structures of Illifunone-C (5c) and Illifunone-D (5d)

Illifunone-C, a colorless oil, $[\alpha]_D$ +60° (in chloroform) and illifunone-D, colorless prisms, mp 167—168 °C, $[\alpha]_D$ +50° (in chloroform), were both obtained only from *I. arborescens*, along with (−)-illicinones (**1b**—**4b**). The spectral data (IR, UV, MS, ^{1}H-NMR, and ^{13}C-NMR) were similar to those of **5a** and **5b** (see Experimental, Tables II and III). The signal of H-3 showed a triplet at δ 1.71 (J=12 Hz) and double doublets at δ 1.89 (J=4, 11 Hz) in illifunone-C and -D, respectively. The ^{1}H-NMR spectra of illifunone-C and -D seemed analogous to those of **5a** and **5b**. From a biogenetic viewpoint, the stereochemistry of the C_5 unit at C-4 could be assumed to be 4*S* (β), as in (−)-illicinones (**1b**—**4b**) contained in the same plant. The structures of illifunone-C and -D could thus be assigned as **5c** and **5d**, respectively, except for the stereochemistry at C-11.

In the illifunones (**5a**—**d**), the configuration of the remaining isopropanol group was finally deduced from the chemical shift values of H-11 in the ^{1}H-NMR spectra. The H-11 signals of illifunone-C (**5c**) at δ 4.68 and illifunone-D (**5d**) at δ 4.66 were found to be lowfield-shifted by about 0.2 ppm compared with those of illifunone-A (**5a**) at δ 4.42 and illifunone-B (**5b**) at δ 4.43. These facts were considered to indicate that the C-4 axial hydroxyl group and H-11 in illifunone-C (**5c**) and -D (**5d**) are located on the same side, whereas those in illifunone-A (**5a**) and -B (**5b**) are on opposite sides.

Thus, we propose that the isopropanol groups in the illifunones (**5a**—**d**) all took the *R* (β) configuration.

Regarding the stereochemistry of the epoxy group of illicinones-C (**3**) and -D (**4**), if we suppose that the formation of illifunones (**5a**—**d**) occurred by concerted cyclization with cleavage of the epoxy group of illicinones (**3**) and (**4**) as described by Grundon *et al.*,[11] illifunone-A (**5a**) should be synthesized biogenetically by cyclization of the intermediate C having an epoxy group of *S* configuration at C-11 (Chart 5). If the intermediate D having *R* configuration at C-11 were cyclized, the isomer E would be produced. Similarly, illifunone-C (**5c**) is obtained from the intermediate F having *S* configuration at C-11. Consequently, since the illifunones (**5a**—**d**) obtained from natural sources are all 11*R* (11α-H) forms, the absolute configuration of the epoxy group at C-11 in illicinones-C (**3**), and -D (**4**) can be assigned to *S*.

TABLE III. ^{13}C-NMR Spectral Data for Illicinones and Illifunones

Carbon No.	1a, b	2a, b	2c	3a	3b	4a	4b	4c	5a	5b	5c	5d
1	186.2	197.9	198.4	186.2	186.0	198.0	197.3	197.9	200.6	202.4	200.6	201.3
2	139.0	42.0	41.9	138.8	139.6	41.7	41.6	41.5	40.5	44.0	39.8	45.2
3	134.1	30.4	31.0	134.2[a)]	133.6	31.2	30.8	31.3	34.2[a)]	34.9[a)]	34.0[a)]	36.2[a)]
4	81.9	82.6	81.6	80.0	79.6	81.9	80.9	80.2	73.3	73.4	75.6	76.7
5	173.3	175.5	175.2	173.4	173.3	175.0	174.4	174.4	180.6	181.3	179.3	180.5
6	98.0	98.7	98.3	98.3	98.1	99.0	99.1	98.6	99.3	99.1	100.0	100.3
7	33.3	35.3[a)]	33.3	33.3	33.3	35.2[a)]	35.2[a)]	34.6	38.0[a)]	37.3[a)]	38.7[a)]	39.0[a)]
8	134.6	135.2	135.9	134.4[a)]	134.2	135.0	134.9	136.3	135.9	136.9	135.6	138.7
9	116.8	117.1	116.8	117.3	117.5	117.1	117.5	117.1	116.5	116.5	116.7	117.0
10	34.7	35.5[a)]	36.2	36.3	35.6	35.5[a)]	35.7[a)]	36.6	39.0[a)]	38.7[a)]	38.7[a)]	41.2[a)]
11	115.8	116.5	116.8	58.9	58.9	59.1	59.1	58.6	90.5	90.7	90.9	92.0
12	137.1	136.2	136.5	58.1	58.1	57.1	57.9	56.9	71.4	71.3	70.3	70.7
13	17.8	18.1	18.3	18.8	18.7	19.0	19.0	19.0	26.8	26.8	24.4	22.0
14	25.7	25.9	25.8	24.5	24.4	24.6	24.4	24.4	26.9	26.8	26.8	26.2
15	97.9	97.3	97.3	97.9	97.9	97.2	97.4	97.5	—	—	—	—

a) Assignments marked with *a*) in the same column could be interchanged.
The assignment was established by the off-resonance and selective decoupling techniques.

Experimental

IR spectra were recorded on a JASCO IR-A-1 spectrometer in chloroform, except where otherwise stated, and UV spectra were determined on a JASCO UNIDEC-1 spectrometer in 95% ethanol. ^{1}H-NMR and ^{13}C-NMR spectra were taken on JEOL PS-100 and JEOL FX-100 spectrometers, respectively in deuteriochloroform. Chemical shifts are given in ppm (δ) with tetramethylsilane as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. MS were recorded on a Hitachi M-52 spectrometer with a direct inlet system operating at an ionization potential of 70 eV. Molecular formulae were determined from the molecular ion in high-resolution mass spectra, which were recorded on a JEOL DX 300 mass spectrometer. Optical rotations were measured on a JASCO DIP-SL automatic polarimeter in chloroform at 23 °C, and CD spectra on a JASCO J-20 spectrometer. Column chromatography was performed with Kieselgel 60 (70—230 mesh, Merck). Thin layer chromatography (TLC) and preparative layer chromatography (PLC) were carried out on plates coated with Kiesel gel 60 F_{254} (Merck) and Kieselgel PF_{254} (Merck).

Isolation of (+)-Illicinones (1a—4a), and Illifunones (5a, b) from *Illicium tashiroi* MAXIM.——The dried leaves (at room temperature, 350 g) of *I. tashiroi* MAXIM. collected on Iriomote island in October, 1979, were extracted with $CHCl_3$ (10 l×4) at room temperature. The extract was concentrated under reduced pressure at 30—35 °C. The residue (40 g) was chromatographed on a column (100×7.5 cm) of silica gel with benzene, $CHCl_3$, and $CHCl_3$–MeOH (10 : 1) successively, giving four oily substances, named 4*S*-(+)-illicinone-A (**1a**), -B (**2a**), -C (**3a**), and 4*R*-(+)-illicinone-D (**4a**). 4*S*-(+)-Illicinone-A (**1a**, 2.5 g) and 4*S*-(+)-illicinone-B (**2a**, 1.2 g) were purified by rechromatography ($CHCl_3$) or PLC ($CHCl_3$) on silica gel, *Rf* 0.49 and 0.41, respectively, on TLC developed with $CHCl_3$. A mixture of 4*S*-(+)-illicinone-C (**3a**, 0.5 g) and 4*R*-(+)-illicinone-D (**4a**, 0.35 g) was separated by PLC [six developments with benzene–ether (20 : 1)]; the products showed almost the same *Rf* value of 0.27 on TLC developed with $CHCl_3$. The fraction eluted with $CHCl_3$–MeOH was purified by PLC [$CHCl_3$–ether (1 : 1)] to give illifunone-A (**5a**, 0.05 g) and illifunone-B (**5b**, 0.035 g).

Isolation of (−)-Illicinones (1b—4b), and Illifunones (5c, d) from *Illicium arborescens* HAY.——The dried leaves (in a drying oven at 40 °C, 500 g) of *I. arborescens* HAYATA collected in April, 1980, at Nanjenshan in Taiwan were extracted with $CHCl_3$ (10 l×4) at room temperature. The extract was concentrated under reduced pressure at 30—35 °C. The residue (35 g) was chromatographed on a column (100×7.5 cm) of silica gel with benzene, $CHCl_3$, and $CHCl_3$–MeOH (10 : 1), successively, giving six oily substances named illicinones from the $CHCl_3$ fraction. 4*R*-(−)-Illicinone-A (**1b**, 3.0 g), -B (**2b**, 1.0 g), -B (**2c**, 0.3 g), -C (**3b**, 1.0 g) were purified by rechromatography (silica gel, $CHCl_3$) or PLC ($CHCl_3$) on silica gel; *Rf* 0.49, 0.41, 0.33, and 0.27, respectively, on TLC developed with $CHCl_3$. 4*S*-(−)-Illicinone-D (**4b**, 0.4 g), and -D (**4c**, 0.2 g) were also purified by PLC [$CHCl_3$–ether (10 : 1)] on silica gel; *Rf* 0.40 and 0.33, respectively, on TLC developed with $CHCl_3$–ether (10 : 1). The fraction eluted with $CHCl_3$–MeOH was purified by PLC [benzene–ether (1 : 5)] to give illifunone-C (**5c**, 0.075 g) and illifunone-D (**5d**, 0.035 g).

4*S*-(+)-Illicinone-A (1a)——Colorless oil, $[\alpha]_D$ +95° (*c*=0.362). IR ν_{max} cm^{-1}: 1665, 1630, 1610. UV λ_{max} nm (ε): 237 (12700), 283 (5500). MS *m/z*: 246 (M^+, 12%), 178 (base peak), 151, 147, 119, 91, and 69.

4*R*-(−)-Illicinone-A (1b)——Colorless oil, $[\alpha]_D$ −92° (*c*=0.460). M^+, 246.1211 (Calcd for $C_{15}H_{18}O_3$, 246.1255). The IR, ^{1}H-NMR, ^{13}C-NMR, and MS were identical with those of **1a**.

2*R*,4*S*-(+)-Illicinone-B (2a)——Colorless oil, $[\alpha]_D$ +140° (*c*=0.468). IR ν_{max} cm^{-1}: 1630. UV λ_{max} nm (ε): 249 (10500), 278 (sh, 1700). MS *m/z*: 248 (M^+, 37%), 246, 180 (base peak), 178, 149, 139, 137, 121, 109, 91, 69.

2*S*,4*R*-(−)-Illicinone-B (2b)——Colorless oil, $[\alpha]_D$ −132° (*c*=0.470). M^+, 248.1421 (Calcd for $C_{15}H_{20}O_3$, 248.1413). The IR, and ^{1}H-NMR spectra were identical with those of **2a**.

2*R*,4*R*-(−)-Illicinone-B (2c)——Colorless oil, $[\alpha]_D$ −165° (*c*=0.780). IR ν_{max} cm^{-1}: 1635. MS *m/z*: 249 (M^++1), 248 (M^+, 6%), 246, 180 (base peak), 149, 139, 137, 121, 109, 91, 69.

4*S*,11*S*-(+)-Illicinone-C (3a)——Colorless oil, $[\alpha]_D$ +128° (*c*=0.300). IR ν_{max} cm^{-1}: 1677, 1640, 1618. UV λ_{max} nm (ε): 241 (14000), 288 (4400). MS *m/z*: 262 (M^+, 14%), 261, 215, 178, 177, 162, 147 (base peak), 119, 91, 69.

4*R*,11*S*-(−)-Illicinone-C (3b)——Colorless oil, $[\alpha]_D$ −108° (*c*=0.356). M^+, 262.1205 (Calcd for $C_{15}H_{18}O_4$, 262.1205). IR ν_{max} cm^{-1}: 1670, 1640, 1615. UV λ_{max} nm (ε): 239 (7600), 289 (2800). MS *m/z*: 262 (M^+, 14%), 232, 204, 194, 189, 178, 162, 147 (base peak), 119, 91, 69.

2*R*,4*R*,11*S*-(+)-Illicinone-D (4a)——Colorless oil, $[\alpha]_D$ +171° (*c*=0.280). IR ν_{max} cm^{-1}: 1635. UV λ_{max} nm (ε): 248 (20000). MS *m/z*: 264 (M^+, 12%), 196, 178, 163, 149, 137, 125 (base peak), 107, 91, 69.

2*S*,4*S*,11*S*-(−)-Illicinone-D (4b)——Colorless oil, $[\alpha]_D$ −145° (*c*=0.200). M^+, 264.1311 (Calcd for $C_{15}H_{20}O_4$, 264.1361). IR ν_{max} cm^{-1}: 1625. UV λ_{max} nm (ε): 248 (14000). MS *m/z*: 264 (M^+, 32%), 196, 178 (base peak), 163, 137, 125, 107, 91, 85, 69.

2*R*,4*S*-(−)-Illicinone-D (4c)——Colorless oil, $[\alpha]_D$ −152° (*c*=0.300). IR ν_{max} cm^{-1}: 1625. UV λ_{max} nm (ε): 250 (14000). MS *m/z*: 265 (M^++1), 264 (M^+, 5%), 196, 178 (base peak), 163, 137, 125, 107, 91, 85, 69.

Illifunone-A (5a)——Colorless needles from $CHCl_3$, mp 107—110 °C, $[\alpha]_D$ −202° (*c*=0.350). IR ν_{max} cm^{-1}: 3590, 3360, 1638, 1175. UV λ_{max} nm: 257. MS *m/z*: 252 (M^+, 65%), 184 (base peak), 170, 163, 139, 123, 111, 95, 72.

***Illifunone-B* (5b)**——Colorless needles from $CHCl_3$, mp 149—151 °C, $[\alpha]_D$ −177° (*c*=0.330). IR ν_{max} cm^{-1}: 3580, 3340, 1625, and 1164. UV λ_{max} nm: 257. MS *m/z*: 252 (M^+, 48%), 184 (base peak), 163, 135, 124, 113, 98, 72.

Illifunone-C (5c)——Colorless oil, $[\alpha]_D$ +60° (c=0.350). M^+, 252.1362 (Calcd for $C_{14}H_{20}O_4$, 252.1362). IR ν_{max} cm^{-1}: 3575, 3370, 1635, 1175. UV λ_{max} nm: 256. MS m/z: 252 (M^+, 72%), 184 (base peak), 163, 124, 113, 98, 72.

Illifunone-D (5d)——Colorless prisms from $CHCl_3$, mp 167—168 °C, $[\alpha]_D$ +50° (c=0.330). IR ν_{max} cm^{-1}: 3575, 3360, 1630, 1175. UV λ_{max} nm: 257. MS m/z: 252 (M^+, 60%), 184 (base peak), 163, 123, 113, 98, 72.

Treatment of 1a with Hydrochloric Acid——A solution of **1a** (0.3 g) and 5% HCl–MeOH (1 ml) in MeOH (3 ml) was stirred for 12 h at room temperature. The reaction mixture was poured into water and extracted with ether. The ether layer was dried over anhyd. $MgSO_4$ and concentrated. The residue was purified by PLC ($CHCl_3$) to give **6** (106 mg), **7** (17 mg), **8** (20 mg), and **9** (36 mg). **8**: Colorless oil. IR ν_{max} cm^{-1}: 3550, 1720, 1640, 1605. ^{1}H-NMR δ: 6.71 (1H, s), 6.47 (1H, s), 5.92 (1H, m), 5.20 (1H, br, OH), 5.04 (1H, m), 4.92 (1H, m), 3.86 (3H, s), 3.78 (3H, s), 3.28 (2H, d, J=7 Hz). MS m/z: 194 (M^+, base peak), 179, 177, 147, 119, 91. **9**: Colorless oil. IR ν_{max} cm^{-1}: 1663, 1638, 1595. ^{1}H-NMR δ: 6.50 (1H, m), 5.93 (1H, s), 5.83 (1H, m), 5.23 (1H, br s), 5.08 (1H, m), 3.81 (3H, s), 3.18 (2H, m). ^{13}C-NMR δ: 191.4 (s), 186.6 (s), 181.8 (s), 148.2 (s), 132.5 (d), 130.6 (d), 118.6 (t), 107.4 (d), 56.1 (q), 32.7 (t). MS m/z: 178 (M^+, 88%), 177 (base peak), 163, 149, 147, 135, 107, 91, 77. Compounds **6** and **7** were shown to be identical with authentic samples prepared by the method of Alexander *et al.*[12]

Treatment of 2b with Sodium Methoxide——A solution of **2b** (200 mg) and NaOMe (50 mg) in MeOH (2 ml) was stirred for 5 h at room temperature, then poured into water and extracted with ether. The ether layer was dried over anhyd. $MgSO_4$ and concentrated. The residue was purified by PLC ($CHCl_3$) to give **11a** (25 mg) and unchanged starting material **2b** (150 mg). **11a**: Colorless oil. IR ν_{max} cm^{-1}: 3570, 1715, 1645, 1605. ^{1}H-NMR δ: 5.72 (1H, m), 5.25 (1H, s), 5.06 (3H, m), 3.73 (3H, s), 2.68—1.88 (7H, m), 1.77 (3H, s), 1.65 (3H, s). MS m/z: 251 (M^++1), 250 (M^+, 8%), 181, 163, 153, 139 (base peak), 124, 109.

Treatment of 2c with Sodium Methoxide——A solution of **2c** (200 mg) and NaOMe (50 mg) in MeOH (2 ml) was stirred for 5 h at room temperature. The reaction mixture was treated in the usual manner to give **2b** (75 mg), **11a** (65 mg), and **11b** (40 mg). Compounds **2b** and **11a** were shown to be identical with authentic samples obtained from the natural source and from **2b** by NaOMe treatment, respectively, by comparisons of IR, ^{1}H-NMR and $[\alpha]_D$. **11b**: Colorless oil. IR ν_{max} cm^{-1}: 3570, 1715, 1650, 1605. ^{1}H-NMR δ: 5.72 (1H, m), 5.29 (1H, s), 5.02 (3H, m), 3.69 (3H, s), 2.82—1.88 (7H, m), 1.74 (3H, s), 1.66 (3H, s). MS m/z: 251 (M^++1), 250 (M^+, 7%), 181, 163, 153, 139 (base peak), 125, 109.

Epoxidation of 1a——A solution of **1a** (100 mg) and *m*-chloroperbenzoic acid (75 mg) in CH_2Cl_2 (5 ml) was stirred for 12 h at room temperature. After concentration, the residue was purified by PLC ($CHCl_3$) to give two epoxidized products. The mixture was separated by repurification with PLC [20 developments with benzene–ether (30 : 1)] to give **3a** (35 mg) and **3c** (30 mg), enantiomer of **3b**. The structures of **3a** and **3c** (enantiomer of **3b**) were confirmed by comparisons of the IR and ^{1}H-NMR spectra and $[\alpha]_D$ with those of **3a** obtained from *I. tashiroi* and **3b** from *I. arborescens*, respectively.

Epoxidation of 1b——Compound **3b** (28 mg) and its diastereoisomer **3d** (33 mg) were obtained from **1b** (100 mg) in a manner similar to that described for **1a**. The structures of **3b** and **3d** (enantiomer of **3a**) were confirmed by comparisons (IR, ^{1}H-NMR, and $[\alpha]_D$) with authentic samples obtained from natural sources.

Epoxidation of 2a——Compounds **4a** (35 mg) and **4d** (enantiomer of **4b**) (35 mg), were obtained from **2a** (100 mg) in a manner similar to that described for **1a** [PLC: benzene–ether (5 : 1)]. The structures were confirmed by comparisons (IR, ^{1}H-NMR, and $[\alpha]_D$) with authentic samples isolated from natural sources.

Epoxidation of 2c——Compounds **4c** (30 mg) and **4e** (35 mg) were obtained from **2c** (100 mg) in a manner similar to that described for **1a** [PLC: benzene–ether (5 : 1)]. The structure of **4c** was confirmed by comparisons (IR, ^{1}H-NMR, and $[\alpha]_D$) with an authentic sample obtained from *I. arborescens*. **4e**: Colorless oil. IR ν_{max} cm^{-1}: 1620. UV λ_{max} nm (ε): 250 (14000). ^{1}H-NMR δ: 5.80 (1H, m), 5.54 (1H, s), 5.43 (1H, s), 5.41 (1H, s), 5.11 (2H, m), 2.93 (1H, dd, J=2, 8 Hz), 2.22 (1H, dd, J=2, 15 Hz), 1.60 (1H, dd, J=8, 15 Hz), 2.78—2.07 (5H, m), 1.34 (3H, s), 1.27 (3H, s). ^{13}C-NMR δ: 198.5 (s), 174.1 (s), 136.5 (d), 116.9 (t), 98.7 (d), 97.1 (t), 80.6 (s), 58.8 (d), 57.1 (s), 42.1 (d), 35.9 (t), 34.0 (t), 31.5 (t), 24.6 (q), 19.0 (q). MS m/z: 265 (M^++1), 264 (M^+, 38%), 196, 178 (base peak), 163, 137, 125, 107, 91, 85, 69.

Sodium Borohydride Reduction of 4*R*-(−)-Illicinone-A (1b)——1) $NaBH_4$ (0.25 g) was added to a solution of **1b** (1 g) in MeOH (25 ml) with ice-cooling. After being stirred at room temperature for 1 h, the reaction mixture was poured into water and extracted with ether. The ether layer was dried over anhyd. $MgSO_4$ and concentrated. The residue was purified by PLC ($CHCl_3$) to give **2b** (0.2 g) and **2c** (0.11 g) and unstable products (0.45 g). Compound **2b**, a colorless oil, $[\alpha]_D$ −133° (c=0.510), was shown to be identical with the enantiomer of 2*R*,4*S*-(+)-illicinone-B (**2a**) by comparisons of the IR and ^{1}H-NMR spectra and optical rotation. Compound **2c**, a colorless oil, $[\alpha]_D$ −165° (c=0.780), was confirmed to be the diastereomer of **2b**, and was identical with an authentic sample obtained from *I. arborescens* (IR, ^{1}H-NMR, and $[\alpha]_D$ comparisons).

The unstable products were treated with silica gel or dilute H_2SO_4 in $CHCl_3$, and purified by PLC ($CHCl_3$) to give safrole (**14**) (175 mg) and 2-hydroxycyclohexenones (**12**) (90 mg) and (**13**) (60 mg). **12**: Colorless oil, $[\alpha]_D$ −116° (c=0.134). IR ν_{max}: 3500, 1670, 1635, 1607. ^{1}H-NMR δ: 6.80 (1H, dt, J=2, 10 Hz), 6.00 (1H, dd, J=3, 10 Hz), 5.72 (1H, m), 5.08 (3H, m), 3.59 (1H, br s, OH), 2.60 (1H, m), 2.30 (6H, m), 1.74 (3H, s), 1.61 (3H, s). ^{13}C-NMR δ: 201.6 (s), 153.6 (d), 135.3 (s), 134.2 (d), 125.7 (d), 117.7 (t), 117.0 (d), 75.4 (s), 40.3 (t), 39.3 (t), 35.6 (d), 35.4 (t), 25.9 (q), 18.0 (q). **13**: Colorless oil, $[\alpha]_D$ +44° (c=0.144). IR ν_{max} cm^{-1}: 3560, 3500, 1668, 1637, 1615. ^{1}H-NMR δ: 6.83 (1H,

dm, $J=10$ Hz), 5.95 (1H, dd, $J=3$, 10 Hz), 5.72 (1H, m), 5.05 (3H, m), 2.80 (2H, m), 2.45—2.04 (6H, m), 1.74 (3H, s), 1.65 (3H, s). ^{13}C-NMR δ: 198.5 (s), 153.7 (d), 135.3 (s), 135.1 (d), 126.4 (d), 117.8 (d), 117.2 (t), 73.8 (s), 38.6 (t×2), 36.4 (t), 33.2 (d), 26.0 (q), 18.0 (q). MS *m/z*: 221 ($M^+ + 1$), 220 (M^+, 2%), 187, 179, 161, 152, 138, 123, 111 (base peak), 69.

2) A mixture of **1b** (200 mg) and $NaBH_4$ (100 mg) in MeOH (10 ml) was refluxed with stirring for 1 h. The reaction mixture was concentrated, then the residue was poured into water and extracted with ether. The ether layer was dried over anhyd. $MgSO_4$ and concentrated. The residue was purified by PLC ($CHCl_3$) to give **2b** (45 mg), unstable products (75 mg), **11a** (12 mg), and **11b** (6.5 mg). Compounds **2b**, **11a**, and **11b** were shown to be identical with authentic samples obtained from natural sources and by the NaOMe treatment of **2c**. Treatment of the unstable products with acid gave **12**, **13**, and **14**, which were identified by comparison with authentic samples prepared by the method described above.

2*R*,4*R*-(+)-2-Hydroxy-2-isopentyl-4-propylcyclohexanone (15)——A solution of **12** (100 mg) in EtOAc (10 mg) was hydrogenated over 5% Pd-C at room temperature under atmospheric pressure until no more hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was dried over anhyd. $MgSO_4$. Compound **15** was obtained by evaporation of the solvent, as a colorless oil, $[\alpha]_D$ +88° ($c=0.744$). IR ν_{max} (CCl_4) cm^{-1}: 3480 and 1705. ^{1}H-NMR δ: 2.53—1.08 (19H, m), 0.92 (3H, s), 0.85 (3H, s). MS *m/z*: 227 ($M^+ + 1$), 226 (M^+, 23%), 209, 182, 170, 155, 127 (base peak), 112, 109. CD (4.78×10^{-4} M, isooctane) $[\theta]^{23}$ (nm): +5900 (286) (positive maximum); (4.42×10^{-4} M, MeOH) $[\theta]^{23}$ (nm): +4860 (285) (positive maximum); (4.96×10^{-4}, DMSO) $[\theta]^{23}$ (nm): +5450 (291) (positive maximum). The CD curve is illustrated in Fig. 1.

2*R*,4*S*-(−)-2-Hydroxy-2-isopentyl-4-propylcyclohexanone (16)——Compound **16** was prepared from **13** in a manner similar to that described for **15**. **16**: Colorless oil, $[\alpha]_D$ −10° ($c=0.784$). IR ν_{max} (CCl_4) cm^{-1}: 3570, 3475, 1705. ^{1}H-NMR δ: 2.87—1.05 (19H, m), 0.92 (3H, s), 0.87 (3H, s). MS *m/z*: 227 ($M^+ + 1$), 226 (M^+, 21%), 209, 191, 182, 169, 155, 127 (base peak), 109. CD (4.78×10^{-4} M, isooctane) $[\theta]^{23}$ (nm): +3140 (288) (positive maximum); (4.25×10^{-4} M, CCl_4) $[\theta]^{23}$ (nm): +3060 (285—287) (positive maximum); (4.96×10^{-4} M, CH_3CN) $[\theta]^{23}$ (nm): +870 (286) (positive maximum), −400 (315—319) (negative maximum); (6.55×10^{-4} M, DMSO) $[\theta]^{23}$ (nm): −1070 (310) (negative maximum); (3.45×10^{-4} M, MeOH) $[\theta]^{23}$ (nm): −1450 (307) (negative maximum). The CD curve is illustrated in Fig. 2.

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References and Notes

1) Part II: K. Yakushijin, T. Tohshima, R. Suzuki, H. Murata, S. -T. Lu, and H. Furukawa, *Chem. Pharm. Bull.*, **31**, 2879 (1983).
2) S. R. Jensen, A. Kjaer, and B. J. Nielsen, *Acta Chem. Scand., Ser. A*, **27**, 367 (1973).
3) M. Ogura, G. A. Cordell, and N. R. Farnsworth, *J. Natural Prod.*, **39**, 255 (1976).
4) M. Ogura, G. A. Cordell, and N. R. Farnsworth, *J. Natural Prod.*, **40**, 157 (1977), and references therein.
5) K. Yakushijin, J. Sekikawa, R. Suzuki, T. Morishita, H. Furukawa, and H. Murata, *Chem. Pharm. Bull.*, **28**, 1951 (1980).
6) K. Yakushijin, R. Suzuki, T. Tohshima, H. Murata, H. Furukawa, T. Nakabayashi, and K. Kurotaki, Abstracts of Papers, the 23rd Symposium of the Chemistry of Natural Products, Nagoya, 1980, p. 648.
7) G. Büchi, P. Chu, A. Hoppmann, C. Mak, and A. Pearce, *J. Org. Chem.*, **43**, 3983 (1978).
8) T. Suga, T. Shishibori, and T. Matsuura, *J. Org. Chem.*, **32**, 965 (1967).
9) T. Suga, T. Shishibori, and T. Matsuura, *Bull. Chem. Soc. Jpn.*, **41**, 944 (1968).
10) Compounds **11a** and **11b** were also obtained by the treatment of 4*R*-(−)-illicinone-A (**1b**) with sodium borohydride in methanol at refluxing temperature.
11) M. F. Grundon and I. S. McColl, *Phytochemistry*, **14**, 143 (1975).
12) B. H. Alexander, S. I. Gestler, R. T. Brown, T. A. Oda, and M. Beroza, *J. Org. Chem.*, **24**, 1504 (1959).