Chem. Pharm. Bull. 32(1) 23-30 (1984)

Studies on the Constituents of the Plants of *Illicium* Species. IV.[1] Thermal and Photochemical Reactions of Illicinone-A, a Novel Phytoquinoid from *Illicium* Plants

KENICHI YAKUSHIJIN,[a] HIROSHI FURUKAWA,*,[a] and ANDREW T. MCPHAIL[b]

Faculty of Pharmacy, Meijo University,[a] Tempaku, Nagoya 468, Japan
and Paul M. Gross Chemical Laboratory, Duke University,[b]
Durham, North Carolina 27706, U.S.A.

(Received April 27, 1983)

Conversion of illicinone-A (**1**) to illicinole (**4**) and the reverse reaction (**4**→**1**) were occurred thermally and photochemically, respectively. The photochemical reaction of illicinone-A (**1**) led to the formation of **5** and **6**, having novel carbon skeletons. The structure of **5** was established by X-ray analysis.

Keywords——illicinone-A; illicinole; thermal reaction; photochemical reaction; X-ray analysis; ^{13}C-NMR; phytoquinoid; *Illicium*

In the preceding paper,[1] we reported the isolation of novel phytoquinoids 4*S*-(+)-illicinone-A and its enantiomer, 4*R*-(−)-illicinone-A (**1**), from leaves of *Illicium tashiroi* and *I. arborescens*, respectively, along with their analogues. Illicinone-A possesses a unique, oxidized 1,3-benzodioxole skeleton bearing an allyl moiety and a prenyl moiety. From the biogenetic viewpoint, an interesting feature of the structure is that it contains the structural units of both lignans [C_6+C_3] and terpenes [C_5]. 4*R*-(−)-Illicinone-A (**1**) and its racemic form were found to show strong repellent activities against sea snail, *Monodonta neritoides*, and *Ulva pertusa* KJELLMAN.[2,3]

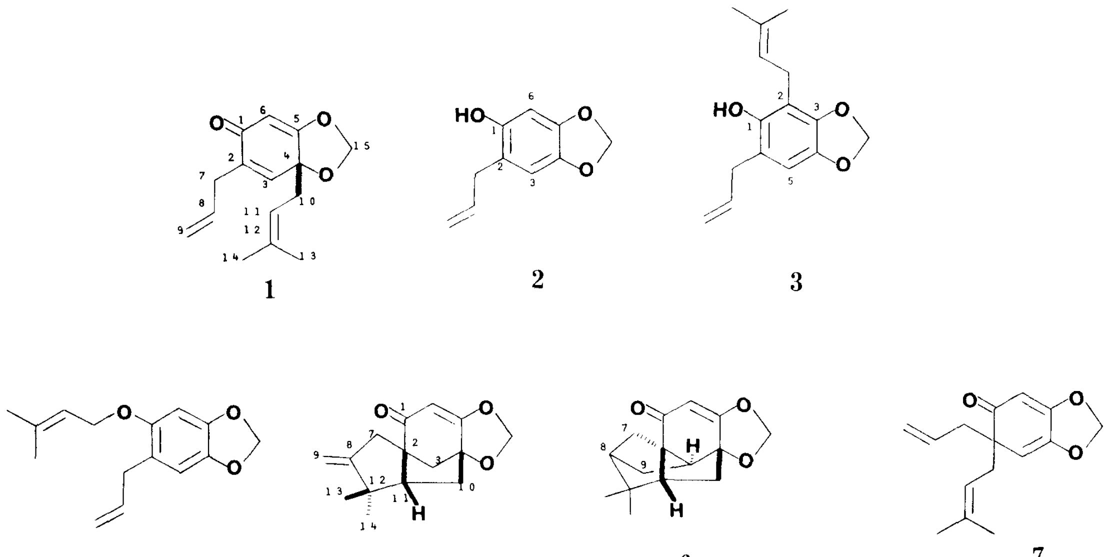
We discribe here the thermal and photochemical reactions of 4*R*-(−)-illicinone-A (**1**).

Results and Discussion

Thermal treatment of 4*R*-(−)-illicinone-A (**1**) at 190—200 °C in a sealed tube for 4 h led to the formation of **2** (31%), **3** (11%), and illicinole (**4**) (13%), one of the constituents of leaves of *Illicium* plants.[4,5] The structures of **2** and **4** were confirmed by direct comparisons of infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectra with those of authentic samples. The structure of **3** was assigned by consideration of the ^{1}H-NMR, carbon-13 nuclear magnetic resonance (^{13}C-NMR), IR, and mass spectra (MS).[6] Compounds **2** and **3** were thought to be formed by the rearrangement of **4** derived from **1**, because thermal reaction of **4** at 190—200 °C in a sealed tube for 4 h also gave **2** and **3** in 50 and 12% yields, respectively.[7]

In these rearrangements, the prenyl group is considered to migrate without isomerization or radical inversion as seen in acid-catalyzed amino Claisen rearrangement.[8] Thus, the transformation from **1** to **4** is considered to be a thermal reaction which is not reversible.

Irradiation of 4*R*-(−)-illicinone-A (**1**) in ether at 20—30 °C with a 400W high-pressure mercury lamp for 1 h afforded two major products as well as a minor product **2** (5%) which were purified by preparative silica gel layer chromatography (PLC) with chloroform–ether (10:1). Compound **5**, one of these products was obtained from chloroform in the form of colorless needles, mp 90—92 °C, $[\alpha]_D$ −23° (in chloroform). Its IR spectrum lacked the



1 2 3

4 5 6 7

Chart 1

TABLE I. ^{13}C-NMR Spectral Data$^{a)}$ for Illicinone-A (**1**) and Its Photochemical Reaction Products (**5** and **6**)

Atom No.	**1**	**5**	**6**	Atom No.	**1**	**5**	**6**
C-1	186.2 (s)	199.7 (s)	199.4 (s)	C-8	134.6 (s)	159.1 (s)	46.9 (d)
C-2	139.0 (s)	56.8 (s)	64.9 (s)	C-9	116.8 (t)	104.9 (t)	33.9 (t)
C-3	134.1 (d)	35.0 (t)	48.1 (d)	C-10	34.7 (t)	31.8 (t)	33.3 (t)
C-4	81.9 (s)	87.5 (s)	90.5 (s)	C-11	115.8 (d)	53.7 (d)	53.1 (d)
C-5	173.3 (s)	177.3 (s)	181.5 (s)	C-12	137.1 (s)	42.7 (s)	41.1 (s)
C-6	98.0 (d)	94.9 (d)	96.6 (d)	C-13	17.8 (q)	24.6 (q)	22.1 (q)
C-7	33.3 (t)	44.7 (t)	27.0 (t)	C-14	25.7 (q)	31.5 (q)	29.6 (q)
				C-15	97.9 (t)	99.1 (t)	99.4 (t)

a) Assignments were established by off-resonance and/or selective decoupling techniques.

characteristic absorption$^{9)}$ of the cross conjugated dienone system present in **1** [$\nu_{\max}$ 1665, 1630, and 1610 cm^{-1}], and contained a band at 1635 cm^{-1} which was indicative of the presence of an α,β-unsaturated carbonyl moiety. The signals in the ^{1}H-NMR spectrum of **1** assigned to the prenyl [δ 1.54 (3H, s), 1.68 (3H, s), 4.95 (1H, m), and 2.43 (2H, d)] and the allyl [δ 5.10 (1H, br s), 4.95 (1H, m), 5.78 (1H, m), and 3.01 (2H, d)] side chains, in addition to that due to the β-proton of the cross-conjugated dienone moiety [δ 6.54 (1H, s)], were absent from the spectrum of **5**. However, in common with the spectrum of **1**, signals due to the α-proton of an α,β-unsaturated carbonyl and two protons of a methylenedioxy group appeared as three one-proton sharp singlets (δ 5.68, 5.50, and 5.30). The presence of an exocyclic double bond and a *gem*-dimethyl group in **5** were indicated, respectively, by a two-proton broad singlets at δ 4.91 and 4.85 which were coupled with H-7 at δ 3.35 (1H, dt, $J=2$, and 16 Hz), and two three-proton singlets at δ 1.14 and 1.11. These assignments were supported by the ^{13}C-NMR spectrum (Table I) of **5** wherein signals due to the two carbon atoms of the exocyclic double bond appeared at δ 104.9 (t) and 159.1 (s), while those due to the *gem*-dimethyl group carbon atoms appeared at δ 31.5 (q), 24.6 (q), and 42.7 (s).

A single-crystal X-ray analysis established the structure of **5** unequivocally. The structure was solved by direct methods.$^{10)}$ Full-matrix least-squares refinement of atomic positional and

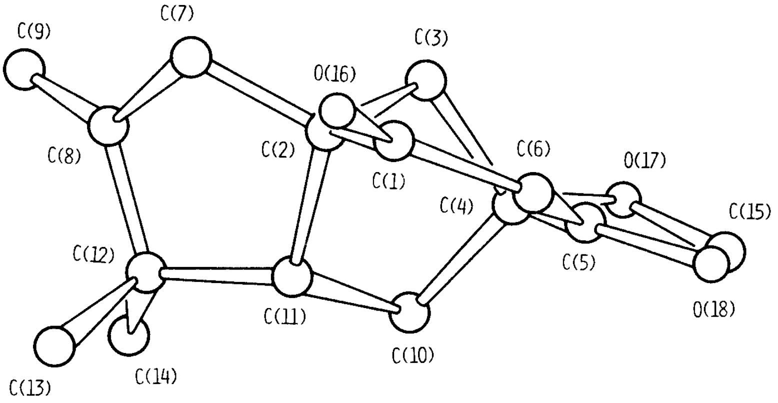


Fig. 1. Structure and Solid-State Conformation of **5**

Table II. Non-hydrogen Atom Fractional Co-ordinates (× 10^3), with Standard Deviations in Parentheses

Atom	*x*	*y*	*z*
C(1)	4050 (8)	7100 (3)	5737 (10)
C(2)	3983 (7)	6770 (3)	3761 (9)
C(3)	3389 (7)	7236 (3)	2230 (9)
C(4)	4641 (7)	7681 (3)	2072 (9)
C(5)	4796 (7)	8028 (3)	3987 (10)
C(6)	4513 (8)	7777 (3)	5687 (10)
C(7)	3286 (8)	6111 (3)	3788 (12)
C(8)	4074 (8)	5750 (3)	2217 (11)
C(9)	3519 (10)	5327 (4)	1040 (16)
C(10)	5872 (7)	7219 (3)	1623 (9)
C(11)	5561 (7)	6659 (3)	3036 (10)
C(12)	5616 (8)	5961 (3)	2220 (13)
C(13)	6471 (11)	5547 (4)	3672 (19)
C(14)	6296 (10)	5897 (4)	181 (15)
C(15)	5337 (10)	8701 (3)	1553 (12)
O(16)	3772 (6)	6823 (3)	7249 (7)
O(17)	4522 (6)	8204 (2)	721 (7)
O(18)	5162 (6)	8639 (2)	3630 (7)

thermal parameters converged to $R=0.059$ for 744 reflections measured with a diffractometer. Final non-hydrogen atom positional and thermal parameters are given in Tables II and III, respectively. A view of the structure with the atom numbering scheme is presented in Fig. 1. Interatomic distances and bond angles are given in Table IV, and torsion angles in Table V.

Bond lengths all lie close to accepted values save for the somewhat elongated C(2)–C(11) and C(11)–C(12) distances [1.581 (10) Å and 1.564 (9) Å, respectively] between tetra- and trisubstituted carbon centers. The cyclohexenone ring approximates to a C_s-envelope (sofa) form with the mirror plane of symmetry passing through C(3) and C(6). Both cyclopentane rings adopt half-chair forms, whereas the 1,3-dioxolane ring has an envelope conformation with O(17) as the out-of-plane atom.

The second major product **6** was obtained as a colorless oil, $[\alpha]_D$ $-19°$ (in chloroform). Its ultraviolet (UV) spectrum was similar to that of **5**, and in its IR spectrum the characteristic α,β-unsaturated carbonyl band appeared at $1632\,cm^{-1}$. In its ^{1}H-NMR spectrum, three one-

Table III. Anisotropic Thermal Parameters[a] (× 10^3), with Standard Deviations in Parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	52 (4)	62 (4)	36 (3)	3 (4)	2 (4)	−8 (4)
C(2)	41 (4)	51 (4)	34 (3)	−7 (3)	5 (3)	−6 (3)
C(3)	46 (4)	54 (4)	31 (3)	7 (4)	−6 (3)	−14 (3)
C(4)	47 (3)	42 (3)	35 (3)	−11 (3)	−5 (4)	−2 (3)
C(5)	42 (4)	54 (4)	43 (4)	2 (4)	−11 (4)	−8 (3)
C(6)	62 (4)	66 (4)	35 (3)	9 (4)	1 (4)	−19 (4)
C(7)	56 (4)	51 (4)	62 (4)	−15 (4)	1 (5)	6 (4)
C(8)	70 (5)	39 (3)	56 (4)	−6 (4)	10 (5)	−2 (4)
C(9)	87 (6)	72 (5)	95 (6)	−15 (5)	4 (6)	−25 (3)
C(10)	50 (4)	39 (3)	42 (3)	−1 (4)	11 (3)	1 (3)
C(11)	37 (4)	45 (3)	48 (4)	4 (3)	−4 (3)	5 (3)
C(12)	52 (4)	40 (3)	86 (6)	13 (3)	5 (5)	9 (4)
C(13)	100 (7)	54 (5)	193 (11)	15 (5)	−53 (8)	31 (5)
C(14)	100 (6)	55 (5)	128 (7)	7 (5)	60 (6)	−21 (5)
C(15)	80 (5)	52 (4)	65 (5)	−2 (5)	−7 (5)	17 (4)
O(16)	101 (4)	88 (4)	36 (2)	1 (4)	17 (3)	5 (3)
O(17)	78 (3)	49 (2)	47 (2)	0 (3)	−15 (3)	16 (2)
O(18)	83 (4)	44 (2)	64 (3)	−10 (3)	−8 (3)	−6 (3)

[a] In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

proton singlets appeared at δ 5.69, 5.47, and 5.31, being similar to those of **5**, and a six-proton singlet due to a *gem*-dimethyl group appeared at δ 1.08. In contrast, signals due to the exocyclic double bond in **5** were absent from the ^{1}H-NMR spectrum of **6**. Comparison of the ^{13}C-NMR spectra of **5** and **6** showed that singlets at δ 159.1 (C-8) and a triplet at δ 44.7 (C-7) as well as a triplet at δ 104.9 (C-9) in the spectrum of **5** were all shifted upfield to δ 46.9 (d), 27.0 (t), and 33.9 (t), respectively, in that of **6**, whereas a triplet at δ 35.0 (C-3) in the former appeared downfield as a doublet (δ 48.1) in the latter, while another triplet at δ 99.1 (C-15) in the spectrum of **5** had a very similar chemical shift to that (δ 99.4) in **6**. Furthermore, when gated decoupling was employed in connection with the three high-field triplets at δ 33.9, 33.3, and 27.0, those at δ 33.3 and 27.0 appeared as a pair of triplets owing to long-range coupling with a single proton, whereas the third signal [δ 33.9 (C-9)] appeared as a triplet accompanied by a fine splitting pattern as a consequence of coupling with two protons. Consideration of these results in conjunction with the probable mechanism (Chart 2) of formation allowed the structure **6** to be assigned to this product.

On the other hand, irradiation of illicinole (**4**) under the same conditions for 30 minutes afforded **1** (19%), **5** (28%), **6** (23%), and **7**$^{5)}$ (12%) as racemates, and **2** (16%). Each compound was identified by comparison of IR, ^{1}H-NMR, ^{13}C-NMR, and/or MS with those of the sample obtained in the preceding reaction.

A similar photochemical treatment of **4** for 10 min gave **1** in 44% yield together with four other products (**2**, **5**, **6**, and **7**), whereas after one hour, the presence of **1** was not observed. These five products are considered to be formed by a dissociation-radical recombination mechanism as described by Carroll *et al.*$^{11)}$

Thus, conversion of illicinole (**4**) to illicinone-A (racemic form of **1**) occurred photochemically while the reverse reaction occurred thermally. Furthermore, the photochemical reaction of illicinone-A (**1**) led to the formation of **5** and **6**, having novel carbon skeletons.

Table IV. Interatomic Distances (Å) and Angles (°), with Standard Deviations in Parentheses

(a) Bond lengths			
C(1)–C(2)	1.517 (9)	C(5)–O(18)	1.347 (8)
C(1)–C(6)	1.483 (10)	C(15)–O(17)	1.411 (9)
C(1)–O(16)	1.213 (8)	C(15)–O(18)	1.435 (9)
C(2)–C(3)	1.534 (9)	C(7)–C(8)	1.506 (11)
C(2)–C(7)	1.527 (10)	C(8)–C(9)	1.305 (12)
C(2)–C(11)	1.581 (10)	C(8)–C(12)	1.516 (11)
C(3)–C(4)	1.506 (9)	C(10)–C(11)	1.546 (9)
C(4)–C(5)	1.502 (9)	C(11)–C(12)	1.564 (9)
C(4)–C(10)	1.539 (9)	C(12)–C(13)	1.543 (13)
C(4)–O(17)	1.435 (8)	C(12)–C(14)	1.538 (13)
C(5)–C(6)	1.302 (9)		
(b) Bond angles			
C(2)–C(1)–C(6)	115.2 (6)	C(1)–C(6)–C(5)	117.7 (6)
C(2)–C(1)–O(16)	122.1 (6)	O(17)–C(15)–C(18)	105.6 (6)
C(6)–C(1)–O(16)	122.6 (6)	C(2)–C(7)–C(8)	103.4 (6)
C(1)–C(2)–C(3)	109.4 (5)	C(7)–C(8)–C(9)	125.6 (8)
C(1)–C(2)–C(7)	114.7 (6)	C(7)–C(8)–C(12)	108.9 (6)
C(1)–C(2)–C(11)	107.8 (5)	C(9)–C(8)–C(12)	125.5 (8)
C(3)–C(2)–C(7)	115.2 (6)	C(4)–C(10)–C(11)	102.0 (5)
C(3)–C(2)–C(11)	102.8 (5)	C(2)–C(11)–C(10)	105.2 (5)
C(7)–C(2)–C(11)	105.9 (5)	C(2)–C(11)–C(12)	106.3 (5)
C(2)–C(3)–C(4)	99.0 (5)	C(10)–C(11)–C(12)	118.5 (6)
C(3)–C(4)–C(5)	108.1 (5)	C(8)–C(12)–C(11)	103.9 (5)
C(3)–C(4)–C(10)	102.3 (5)	C(8)–C(12)–C(13)	109.7 (6)
C(3)–C(4)–O(17)	117.2 (5)	C(8)–C(12)–C(14)	111.8 (7)
C(5)–C(4)–C(10)	113.8 (5)	C(11)–C(12)–C(13)	108.2 (7)
C(5)–C(4)–O(17)	101.5 (5)	C(11)–C(12)–C(14)	114.7 (6)
C(10)–C(4)–O(17)	114.1 (5)	C(13)–C(12)–C(14)	108.5 (7)
C(4)–C(5)–C(6)	124.3 (6)	C(4)–O(17)–C(15)	105.1 (5)
C(4)–C(5)–O(18)	109.0 (5)	C(5)–O(18)–C(15)	107.1 (5)
C(6)–C(5)–O(18)	126.6 (6)		

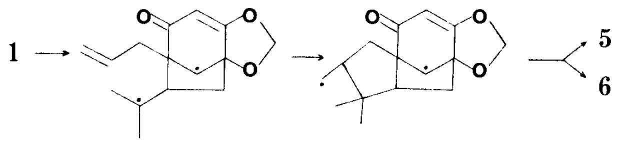


Chart 2

Experimental

IR spectra were recorded on a JASCO IR-A-1 spectrometer in chloroform, and UV spectra were determined on a JASCO UVIDEC-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 ions in high-resolution MS, 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. 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 Kieselgel 60 F_{254} (Merck) and Kieselgel PF_{254} (Merck), respectively.

Thermal Reaction of 4*R*-(−)-Illicinone-A (1)——A solution of **1** (0.2 g) in dimethyl formamide (DMF) (2 ml) was

TABLE V. Torsion Angles[a] (°), with Standard Deviations in Parentheses

C(6)–C(1)–C(2)–C(3)	−39.6 (6)	C(3)–C(4)–C(10)–C(11)	−42.3 (5)
C(6)–C(1)–C(2)–C(7)	−170.8 (6)	C(5)–C(4)–C(10)–C(11)	74.1 (5)
C(6)–C(1)–C(2)–C(11)	71.5 (6)	O(17)–C(4)–C(10)–C(11)	−169.9 (5)
O(16)–C(1)–C(2)–C(3)	141.8 (7)	C(3)–C(4)–O(17)–C(15)	148.6 (5)
O(16)–C(1)–C(2)–C(7)	10.6 (8)	C(5)–C(4)–O(17)–C(15)	31.1 (6)
O(16)–C(1)–C(2)–C(11)	−107.1 (7)	C(10)–C(4)–O(17)–C(15)	−91.8 (5)
C(2)–C(1)–C(6)–C(5)	0.9 (7)	C(4)–C(5)–C(6)–C(1)	1.9 (7)
O(16)–C(1)–C(6)–C(5)	179.5 (7)	O(18)–C(5)–C(6)–C(1)	176.6 (8)
C(1)–C(2)–C(3)–C(4)	71.1 (5)	C(6)–C(5)–O(18)–C(15)	−178.6 (6)
C(7)–C(2)–C(3)–C(4)	−158.0 (5)	C(4)–C(5)–O(18)–C(15)	−3.3 (6)
C(11)–C(2)–C(3)–C(4)	−43.3 (5)	O(18)–C(15)–O(17)–C(4)	−34.6 (5)
C(1)–C(2)–C(7)–C(8)	−147.4 (6)	O(17)–C(15)–O(18)–C(5)	23.4 (6)
C(3)–C(2)–C(7)–C(8)	84.3 (6)	C(2)–C(7)–C(8)–C(9)	−144.3 (8)
C(11)–C(2)–C(7)–C(8)	−28.6 (6)	C(2)–C(7)–C(8)–C(12)	35.6 (6)
C(1)–C(2)–C(11)–C(10)	−97.7 (5)	C(7)–C(8)–C(12)–C(11)	−27.4 (6)
C(1)–C(2)–C(11)–C(12)	135.8 (5)	C(7)–C(8)–C(12)–C(13)	88.0 (7)
C(3)–C(2)–C(11)–C(10)	17.9 (5)	C(7)–C(8)–C(12)–C(14)	−151.6 (7)
C(2)–C(3)–C(11)–C(12)	−108.7 (5)	C(9)–C(8)–C(12)–C(11)	152.5 (8)
C(7)–C(2)–C(11)–C(10)	139.1 (5)	C(9)–C(8)–C(12)–C(13)	−92.1 (8)
C(7)–C(2)–C(11)–C(12)	12.6 (6)	C(9)–C(8)–C(12)–C(14)	28.3 (8)
C(2)–C(3)–C(4)–C(5)	−66.7 (5)	C(4)–C(10)–C(11)–C(2)	14.2 (5)
C(2)–C(3)–C(4)–C(10)	53.8 (5)	C(4)–C(10)–C(11)–C(12)	132.7 (6)
C(2)–C(3)–C(4)–O(17)	179.4 (5)	C(2)–C(11)–C(12)–C(8)	8.4 (6)
C(3)–C(4)–C(5)–C(6)	34.3 (6)	C(2)–C(11)–C(12)–C(13)	−108.1 (6)
C(3)–C(4)–C(5)–O(18)	−141.1 (5)	C(2)–C(11)–C(12)–C(14)	130.7 (7)
C(10)–C(4)–C(5)–C(6)	−78.7 (6)	C(10)–C(11)–C(12)–C(8)	−109.6 (6)
C(10)–C(4)–C(5)–O(18)	105.9 (6)	C(10)–C(11)–C(12)–C(13)	133.9 (7)
O(17)–C(4)–C(5)–C(6)	158.2 (6)	C(10)–C(11)–C(12)–C(14)	12.7 (7)
O(17)–C(4)–C(5)–O(18)	−17.2 (5)		

[a] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D.

heated in a sealed tube at 190—200 °C for 4 h. The reaction mixture was poured into water and extracted with ether. The ether extract was dried over anhyd. $MgSO_4$ and concentrated. The residue was purified by PLC [benzene–$CHCl_3$ (1 : 1)] to give **2** (31%), **3** (11%), and **4** (13%). Compounds **2** and **4** were shown to be identical with synthetic[12)] and natural[4)] samples, respectively, by comparisons of the IR and ^{1}H-NMR spectra. Compound **3** was obtained as colorless needles, mp 93—96 °C. IR ν_{max} cm^{-1}: 3450 and 1635. UV λ_{max} nm (ε): 239 (4000), 298 (3900). MS *m/z*: 246 (M$^+$, base peak), 299, 190, 160, 132, 91. ^{1}H-NMR δ: 6.41 (1H, s), 5.90 (1H, m), 5.82 (2H, s), 5.12 (3H, m), 3.29 (4H, m), 1.79 (3H, s), 1.75 (3H, s). ^{13}C-NMR δ: 147.0 (2 × s), 140.2 (s), 136.5 (d), 134.5 (s), 120.8 (d), 117.2 (s), 115.6 (t), 110.7 (s), 106.9 (d), 100.4 (t), 34.9 (t), 25.7 (q), 23.4 (t), 18.8 (q).

Thermal Reaction of Illicinole (4)——Illicinole (**4**) (0.1 g) was heated in a sealed tube at 190—200 °C for 4 h. The reaction mixture was purified by PLC [benzene–hexane (1 : 1)] to give **2** (50%) and **3** (12%). Each compound was shown to be identical with the corresponding product obtained by thermal reaction of **1** by IR, ^{1}H-NMR, and mass spectral comparisons.

Photochemical Reaction of 4*R*-(−)-Illicinone-A (1)——A solution of **1** (0.1 g) in ether (200 ml) was irradiated at 20—30 °C for 1 h. After removal of the solvent, the residue was purified by PLC [$CHCl_3$–ether (10 : 1)] to give **2** (5%), **5** (24%), and **6** (21%). Compound **2** was shown to be identical with an authentic sample by IR, ^{1}H-NMR and mass spectral comparisons. **5**: Colorless needles from $CHCl_3$, mp 90—92 °C, $[\alpha]_D$ −23 ° (c = 0.46). M$^+$, 246.1239 (Calcd for $C_{15}H_{18}O_3$, 246.1255). IR ν_{max} cm^{-1}: 1635. UV λ_{max} nm (ε): 246 (12500). ^{1}H-NMR δ: 5.68 (1H, s), 5.50 (1H, s), 5.30 (1H, s), 4.91 (1H, br s), 4.85 (1H, br s), 3.35 (1H, dt, J = 2 and 16 Hz), 2.20—1.84 (6H, m), 1.14 (3H, s), 1.11 (3H, s). MS *m/z*: 246 (M$^+$), 231, 216, 201, 188, 173, 147, 125, 91. **6**: Colorless oil, $[\alpha]_D$ −19 ° (c = 0.52). M$^+$, 246.1214 (Calcd for $C_{15}H_{18}O_3$, 246.1255). IR ν_{max} cm^{-1}: 1632. UV λ_{max} nm (ε): 248 (12000). ^{1}H-NMR δ: 5.69 (1H, s), 5.47 (1H, s), 5.31 (1H, s), 2.36—1.39 (9H, m), 1.08 (6H, s). MS *m/z*: 246 (M$^+$), 231, 218, 203, 176, 147, 125, 105, 91.

Photochemical Reaction of Illicinole (4)——a) A solution of **4** (0.1 g) in ether (200 ml) was irradiated at 20—30 °C for 30 min. After concentration, the residue was purified by PLC [$CHCl_3$–ether (10 : 1)] to give **1** (7%), **2** (9%), **5**

(10%), **6** (8%), and **7** (7%).

b) In the reaction of **4** for 10 min, the yields of the products **1**, **2**, **5**, **6**, and **7** were 20, 10, 5, 11, and 6%, respectively.

c) In the reaction of **4** for 1 h, **5** and **6** were obtained in 7 and 6% yields, respectively, and the other products were not obtained. The structure of all products were confirmed by comparison with corresponding samples obtained in the preceding reactions (IR, ^{1}H-NMR and TLC comparisons).

Crystals of **5**, in the form of thin plates, were grown from methanol.

Crystal Data——$C_{15}H_{18}O_3$ (**5**), $M=246.31$, orthorhomic, $a=9.403$ (4), $b=20.911$ (8), $c=6.831$ (3) Å, $U=1343.2$ Å^3, $Z=4$, $D_{\text{calc.}}=1.218\ \text{g}\cdot\text{cm}^{-3}$. Absorption coefficient for Cu-K_α radiation ($\lambda=1.5418$ Å), $\mu=6.9\ \text{cm}^{-1}$. Space group $P2_12_12_1(D_2^4)$ was uniquely determined from systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, $00l$ when $l \neq 2n$.

Crystallographic Measurements——A crystal of dimensions *ca.* 0.05 × 0.28 × 0.80 mm was mounted on the end of a thin glass fibre. Oscillation and Weissenberg photographs taken with Cu-K_α radiation yielded preliminary unit-cell parameters and space group information. Intensity data for one octant of reciprocal space to $\theta=67°$ were recorded on an Enraf–Nonius CAD-3 automated diffractometer (Ni-filtered Cu-K_α radiation; θ–2θ scans) as described in detail elsewhere.[13] A total of 744 reflections for which $I>2.0\sigma(I)[\sigma^2(I)=\text{scan count}+\text{total background count}]$ were considered as observed and were retained for structure analysis and refinement. These data were corrected for Lorentz and polarization effects but not for the small effects of absorption. Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 40 reflections ($29°<\theta<43°$) widely separated in reciprocal space.

Structure Analysis——The structure was solved by direct methods using the MULTAN76[10] suite of programs with the 250 largest $|E|$-values. A fourteen-atom molecular fragment was recognized in an E-map evaluated by use of that set of phase angles which yielded the highest combined figure-of-merit. An F_o Fourier synthesis phased by this fragment ($R=0.34$) furnished approximate positions for the remaining non-hydrogen atoms. During the subsequent full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic thermal parameters, hydrogen atoms were included in the later cycles at their calculated positions. The refinement converged to $R=0.059$. Final non-hydrogen atom positional and thermal parameters are given in Tables II and III.

For the structure–factor calculations, atomic scattering factors for oxygen and carbon were taken from ref. 14, and for hydrogen from ref. 15. In the least-squares iterations, $\sum w\Delta^2$ ($\Delta=||F_o|-|F_c||$) was minimized with $\sqrt{w}=1$ for $|F_o|\leq 20.0$ and $\sqrt{w}=20.0/|F_o|$ for $|F_o|>20.0$; this scheme yielded no systematic dependence of $\langle\sum w\Delta^2\rangle$ when analyzed in ranges of $|F_o|$ and $\sin\theta$.

Acknowledgement We thank Dr. M. Haruna of our University for measurement of ^{13}C-NMR spectra with gated decoupling and for valuable suggestions and discussions, and Professor J. Sakakibara of Nagoya City University for high-resolution mass spectral measurements. Crystallographic calculations, performed at the Triangle Universities Computation Center, North Carolina, were supported by a grant of computer time from Duke University.

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