Tetrahedron, Supplement No. 7, pp. 219 to 225. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON SESQUITERPENOIDS—XII

STRUCTURE AND ABSOLUTE CONFIGURATION OF OPLOPANONE, A NEW SESQUITERPENE FROM *OPLOPANAX JAPONICUS* (NAKAI) NAKAI[2]

KEN'ICHI TAKEDA,† H. MINATO and M. ISHIKAWA
Shionogi Research Laboratory, Shionogi & Co. Ltd., Fukushima-ku, Osaka, Japan

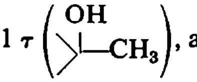
(*Received* 26 *November* 1965)

Abstract—Oplopanone, a new sesquiterpene alcohol, has been isolated from *Oplopanax japonicus* (NAKAI) NAKAI, and represented by formula I. Its absolute configuration is also discussed.

Oplopanax japonicus (NAKAI) NAKAI (Japanese name "Haribuki") a shrub belonging to *Araliaceae* grows in the mountains at the northern part of central Japan and is used as an antipyretic or cough cure.

Although Kariyone and Morotomi[3] isolated echinopanacen, a sesquiterpene, $C_{15}H_{24}$, and echinopanacol, a sesquiterpene alcohol, $C_{15}H_{25}OH$, from the whole plant, the structures of these compounds were not established.

A new type of sesquiterpene ketone, oplopanone (I), $C_{15}H_{26}O_2$, m.p. 96–97°, $[\alpha]_D$ −20·0°, has been isolated from the ether extract of this plant, and its structure and absolute configuration are described in this paper.

Oplopanone (I) shows frequencies at 3583 (OH) and 1711 cm^{-1} (ketonic C═O) in the IR spectrum and methyl signals at 7·82 τ (CH_3CO—), 8·81 τ  $\left(\overset{OH}{>\!|\!-CH_3}\right)$, and 9·06, 9·16, 9·26 and 9·36 τ (isopropyl group) in the NMR spectrum. Moreover, as oplopanone gives iodoform by sodium hypoiodite oxidation and resists acetylation with acetic anhydride–pyridine at room temperature, it is a bicyclic sesquiterpene having an acetyl group and a tertiary hydroxyl group. The structure of the ring bearing an acetyl group was first examined.

Oxidation of oplopanone with trifluoroperacetic acid gave an oily mixture of IIb and IIc (ν_{max} 1781 and 1727 cm^{-1}). This mixture was immediately hydrolysed with 5% potassium hydroxide in methanol to a dihydroxy compound (IIa), m.p. 146–148°. Oxidation of IIa with chromium trioxide afforded a ketone (IV), m.p. 90·5–91·5°, which showed a frequency at 1730 cm^{-1} corresponding to a five-membered ring ketone. This ketone (IV) was stable to alkali* and by reduction with LAH or $NaBH_4$ gave the parent alcohol (IIa) and its epimer (IIIa), m.p. 182–184°, at the ratio of ca. 10:1. The ring having an acetyl group is, therefore five-membered. On treatment of IV with benzaldehyde, it afforded a benzylidene compound (V), m.p. 176–177°, λ_{max} 295 mμ (ε 30,000) in good yield.

† This paper is dedicated to the memory of Professor H. Stephen.

* On reflux of IV in 5% sodium methoxide in methanol for 3 hr, the starting material was recovered.

[1] Part XI, H. Minato and I. Horibe, *J. Chem. Soc.* 7009 (1965).

[2] Preliminary communication, *Chem. Commun.* 79 (1965).

[3] T. Kariyone and S. Morotomi, *J. Pharm. Soc. Japan* 47, 671 (1927).

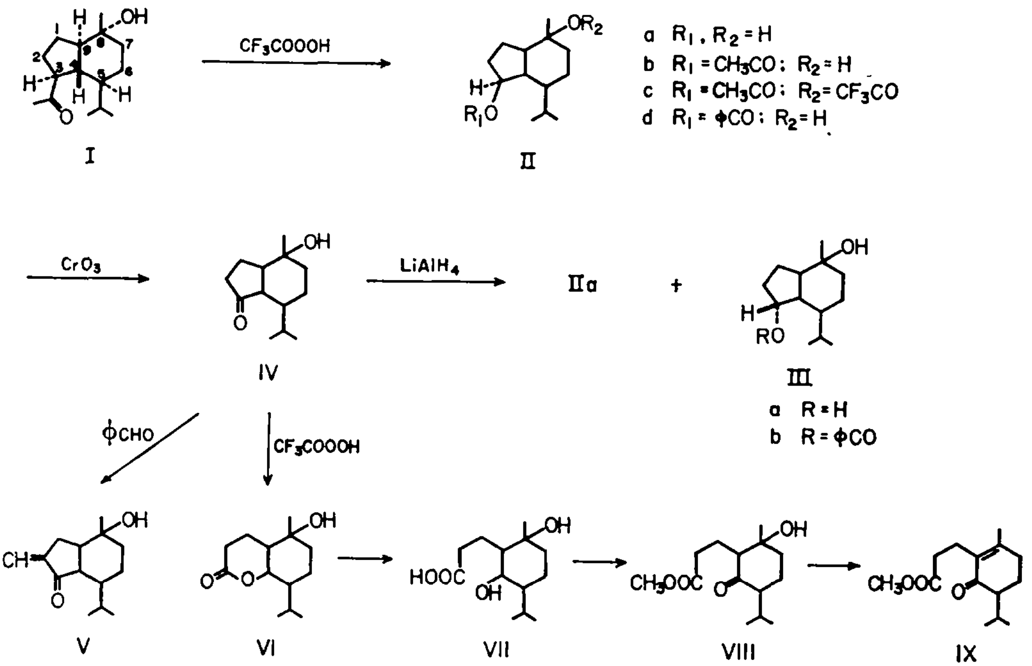


Chart I

This result showed that IV has an active methylene group. Further oxidation of IV with trifluoroperacetic acid gave a δ-lactone (VI), m.p. 114–115°, ν_{max} 1727 cm^{-1}, which showed a triplet signal (J = 8·5 c/s) due to one proton attached to the carbon atom carrying the lactonic oxygen at 6·13 τ in the NMR spectrum. The corresponding hydroxy-acid (VII) was oxidized with chromium trioxide in acetic acid to give a keto-acid together with the δ-lactone (VI), and the former was immediately converted into a keto-ester (VIII), ν_{max} 1735 and 1716 cm^{-1}, by treatment with diazomethane.

As there is only one proton at the carbon atom carrying the lactonic oxygen in the δ-lactone (VI), the carbonyl group corresponding to 1716 cm^{-1} in VIII is a ketonic carbonyl and VIII may be a six-membered ring ketone.

As this keto-ester (VIII) was partly dehydrated to give an α,β-unsaturated ketone (IX) by treatment with neutral alumina in benzene, VIII was used for the following reaction without purification. When compound VIII was refluxed with 5% potassium carbonate in methanol for 1·5 hr and the product esterified with diazomethane, it afforded an oily α,β-unsaturated ketone (IX), λ_{max} 245 mμ (ε 10,200), ν_{max} 1670 and 1637 cm^{-1}, which showed signals for a methyl group on a double bond (8·04 τ) and an isopropyl group (9·10 τ) but no vinyl protons in the NMR spectrum. Therefore, this unsaturated ketone system of IX has a tetrasubstituted ethylenic double bond having one methyl group, but the isopropyl group[*] may not take part in this

---

[*] The isopropyl group of X appeared at 8·89 τ (doublet, J = 6·8 c/s) in the NMR spectrum [H. Hikino, Y. Hikino, Y. Takeshita, K. Meguro and T. Takemoto, *Chem. Pharm. Bull. Tokyo* **11**, 1207 (1963)].

system. From the fact that the tertiary hydroxyl group of VIII was easily dehydrated to give IX by treatment with alumina, this tertiary hydroxyl group is situated at β-position of the ketonic carbonyl group in VIII. Hence two structures (XIII and XIV) must be considered.

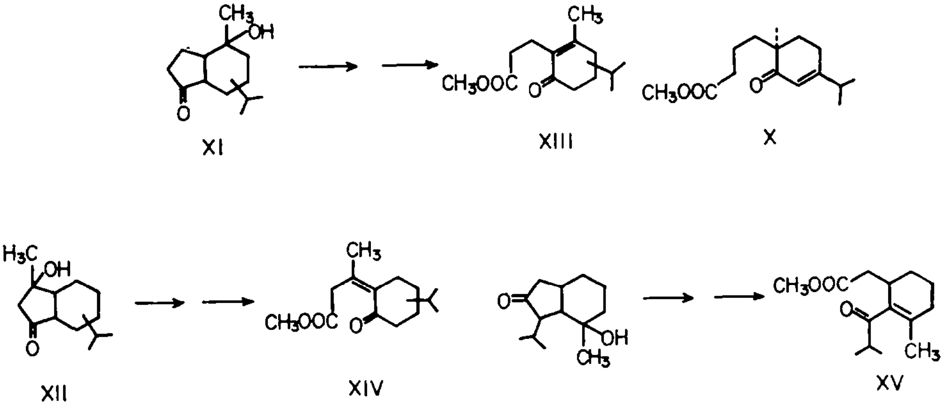


Chart 2

If compound IX is represented by XIII or XIV, compound IV has the structure XI or XII, respectively. As compound IV is stable to an alkali and since XII would easily give an α,β-unsaturated ketone on treatment with alkali, the structure XIV must be excluded for compound IX.

Although structure XV may be regarded as correct for compound IX, the above-mentioned results and the conception of the biogenesis of the sesquiterpene, suggest that oplopanone belongs to a modified cadinane type sesquiterpene.

Oplopanone (I) was reduced with LAH to a mixture of the corresponding alcohol (XVI), m.p. 203–204°, and its amorphous epimer. When this alcoholic mixture was refluxed with methanesulphonyl chloride in pyridine for 3 hr, a mixture of the double bond isomers (XVII and XVIII) was obtained. Osmium tetroxide oxidation of this mixture, afforded isomeric trihydroxy compounds, XIXa, m.p. 202–204°, XIXb, m.p. 173–175°, and XX, m.p. 142·5–144°, in 23%, 20% and 4% yield, respectively. The structures of these three trihydroxy compounds were established by the fact that XIXa and XIXb gave ketone (IV), while XX gave an oily aldehyde (XXI), ν_{max} 2730 and 1722 cm^{-1}, on oxidation with sodium periodate. Treatment of XIXa or XIXb with methanesulphonyl chloride in pyridine afforded the ketone XXII, m.p. 131·5–133·5°, or XXIII, m.p. 109–110°, respectively, and the former was quantitatively isomerized to the latter by treatment with 1% sodium hydroxide in methanol.

When ketone XXII was dehydrated with thionyl chloride in pyridine followed by dehydrogenation with 10% Pd-C at 310°, it gave a naphthol derivative (XXIV) a trinitrobenzene adduct, m.p. 132–134°, which was shown to be identical with 8-isopropyl-2,5-dimethyl-1-naphthol.[4]

Moreover, the ketone XXIII was identical with the compound* synthesized from

* The authors are very grateful to Prof. F. Šorm for sending them a sample of this compound.

[4] K. Takeda, H. Minato and S. Nosaka, *Tetrahedron* 13, 308 (1961).

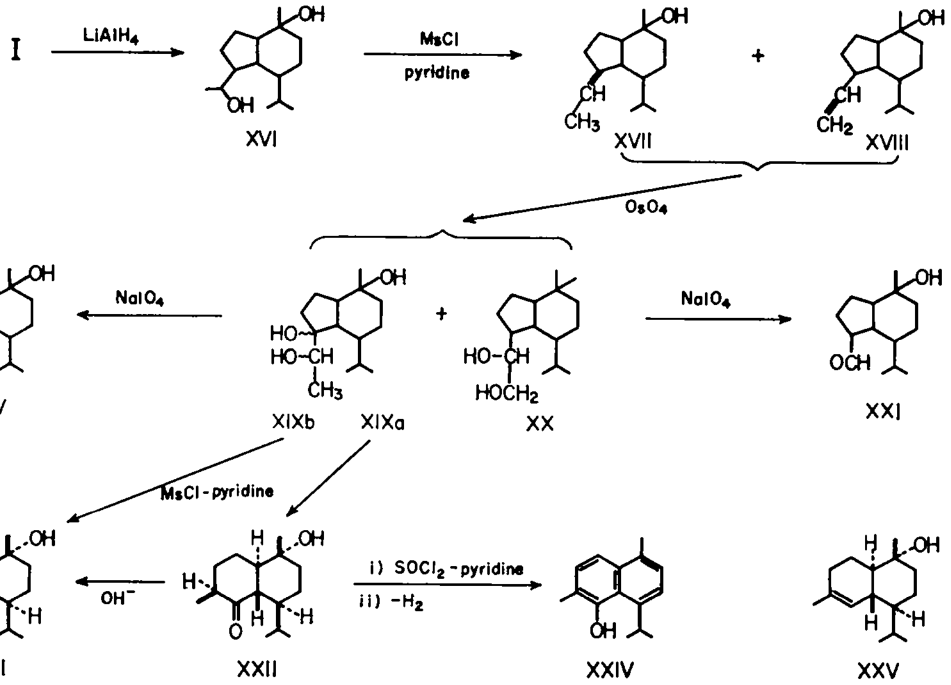


Chart 3

α-cadinol (XXV) by Herout and Sykora[5] by comparison of IR spectra and $[\alpha]_D$ values, and by mixed m.p. determination.

Since the ketone XXIII was obtained from α-cadinol (XXV), the absolute configuration[5] of which had been completely elucidated, the stereochemistry of oplopanone (I) was clarified, except for the configuration at C-3 and C-4. The configuration at C-4 in oplopanone (I) is established by the following observations:

(1) The alcohol (IIa) having the same configuration as oplopanone at C-4 was also obtained by LAH reduction of the ketone (IV), which is stable to alkali.

(2) An optical rotatory dispersion study of IV shows a positive Cotton effect[6] ($a = +179$). The hydrogen at C-4 in IV or oplopanone should, therefore, be β-oriented.*

As the Baeyer–Villiger reaction proceeds with retention of configuration of the migrating group, the configuration at C-3 in oplopanone is also determined by elucidation of that in the alcohol (IIa), which was obtained by this oxidation reaction. As shown in the Table, application of the benzoate rule[7] to the alcohol (IIa) or its epimer (IIIa) indicates that the hydroxyl group at C-3 in IIa is β-oriented* and in IIIa is α-oriented.

---

* The CD of oplopanone (I) and the ketone (IV) were kindly determined by Dr. S. Munavalli (Strasbourg University), and we are very much indebted to him for giving us the information, the results of the CD study gave further support of our determination of the stereochemistry at C-3 and -4 of oplopanone (I).

[5] V. Herout and V. Sykora, *Tetrahedron* 4, 246 (1958).

[6] W. Klyne, *Tetrahedron* 13, 29 (1961).

[7] J. H. Brewster, *Tetrahedron* 13, 106 (1961).

	$[M]_D$ of benzoate	$[M]_D$ of alcohol	$\Delta[M]_D$
IIa	+238	−28	+266
IIIa	−282	−147	−135

This result is further supported by the fact that oplopanone (I) shows a negative Cotton effect[8] (a = −62) by ORD study.

From these results, the structure and the absolute configuration of oplopanone should be represented by formula I.

It is interesting to note that oplopanone belongs to a new type of the modified cadinane sesquiterpene; in the plant body, α-cadinol seems to be a precurser of oplopanone and the former may be converted to oplopanone by ring contraction.

EXPERIMENTAL

NMR spectra were taken on $CDCl_3$ solution with a Varian A-60 NMR Spectrometer. ORD measurements were performed in dioxan solution by means of a Rudolph Recording Spectropolarimeter, Model 260/655/850/810-614. M.ps were taken on a Kofler block and corrected. Unless otherwise stated, UV spectra were taken in 95% EtOH, IR spectra in $CHCl_3$, and rotations in dioxan.

Isolation of oplopanone (I) *from the plant.* The dried and sliced root of *Oplopanax japonicus* (NAKAI) NAKAI (1 kg) was extracted with ether (4 l. × 3) at room temp for 5 days. The combined ether solution was evaporated to leave oily residue (40·77 g). The residue was dissolved in ether (500 ml), washed with 2N HCl, 2N Na_2CO_3 and 2N NaOH, and evaporated leaving an oily neutral residue (28·2 g). The residue was extracted with light petroleum and the extract (22·2 g) was further extracted with 90% EtOH to give an oil (11·7 g). This oil was refluxed with Girard reagent T (2·5 g) in EtOH (70 ml)–acetic acid (7 ml) for 46 hr under N_2 to give the ketonic compound (810 mg) and the non-ketonic compound (9·8 g). The former was chromatographed on neutral Alumina (Activity II) to give oplopanone (I, 206 mg) as colourless prisms (from ether–light petroleum), m.p. 96–97°, $[\alpha]_D^{25\cdot5}$ −20·0° (±4°) (*c*, 0·571), ν_{max} 3583 and 1711 cm^{-1}, NMR 7·82 τ (CH_3CO—), 8·81 τ $\left(-\overset{|}{\underset{\substack{|\\ OH}}{C}}-CH_3\right)$ and 9·06, 9·16, 9·26, 9·36 τ $\left(-CH\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}\right)$, ORD of I: $[\alpha]_{700}$ −10°, $[\alpha]_{308\cdot5}$ −998°, $[\alpha]_{256}$ +1594°, $[\alpha]_{240}$ +1310° (*c*, 0·571; temp 25°). (Found: C, 75·59; H, 11·01; M, 247. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 11·00%; M, 238·4.)

Trifluoroperacetic acid oxidation of opolpanone (I). A solution of trifluoroperacetic acid was prepared by dropwise addition of a solution of trifluoroacetic anhydride (1·3 g, 6 equiv) in dichloromethane (6·5 ml) to a suspension of 80% H_2O_2 (220 mg, 5 equiv) in dichloromethane (1 ml) with stirring in an ice-bath. This peracid solution was added dropwise to a solution of I (246 mg) in dichloromethane (7·5 ml) with stirring in an ice-bath and left for 22 hr at room temp. The mixture was washed with water, 2N Na_2CO_3 and $NaHSO_3$ solution, dried (Na_2SO_4), and evaporated leaving a colourless oil (IIb + IIc) (270 mg), ν_{max} 1781 and 1727 cm^{-1}, which was hydrolysed with 5% KOH–MeOH to give IIa (98 mg) as colourless needles (from acetone), m.p. 146–148°, $[\alpha]_D^{24}$ −13·0° (±4°) (*c*, 0·5016), $[M]_D$ −27·6°, ν_{max}^{Nujol} 3314 cm^{-1}. (Found: C, 73·32; H, 11·38. $C_{13}H_{24}O_2$ requires: C, 73·53; H, 11·39%); monoacetate (IIb), a colourless oil, b.p. 95°–98°/0·1 mm, $[\alpha]_D^{24}$ +15·8° (±4°) (*c*, 0·4885), ν_{max}^{film} 1732 cm^{-1} (Found: C, 70·97; H, 10·43. $C_{15}H_{26}O_3$ requires: C, 70·83; H, 10·30%); monobenzoate (IId), a colourless oil, b.p. 125–130°/0·8 mm, $[\alpha]_D^{24}$ +75·3° (±3·5°) (*c*, 0·640), $[M]_D$ +238°.

Oxidation of IIa *with chromium trioxide.* Jones' reagent* (1·34 ml) was added to a solution of IIa (378 mg) in acetone (20 ml) in an ice-bath with stirring during 1 min and stirred for 4 min at room temp. The mixture was poured into ice-water and extracted with ether giving IV (204 mg) as colourless plates (from ether–light petroleum), m.p. 90·5–91·5°, $[\alpha]_D^{25}$ +69·7° (±4°) (*c*, 0·545), ν_{max} 3514 and

---

* Chromium trioxide (2·67 g) and conc H_2SO_4 (2·3 ml) in water (10 ml).

[8] P. Crabbé, *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* pp. 134–137. Holden-Day (1965).

1730 cm^{-1}, ORD of IV: $[\alpha]_{700}$ +30°, $[\alpha]_{324}$ +3910°, $[\alpha]_{277}$ −4630°, $[\alpha]_{250}$ −3410° (*c*, 0·545; temp 25°). (Found: C, 74·43; H, 10·80. $C_{13}H_{22}O_2$ requires: C, 74·24; H, 10·54%.)

Lithium aluminium hydride reduction of IV. A solution of IV (164 mg) in dry ether (10 ml) was added dropwise to a suspension of LAH (75 mg) in dry ether (10 ml) with stirring in an ice-bath and stirred for 30 min at room temp. To this mixture was added 2N HCl, and then the mixture was extracted with ether, washed with 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving a crystalline substance (163 mg), which was chromatographed on alumina to give IIa (143 mg) and its epimer (IIIa, 12·2 mg), colourless plates, m.p. 182–184°, $[\alpha]_D^{25}$ −69·3° (±4°) (*c*, 0·573), $[M]_D$ −147°. (Found: C, 73·49; H, 11·47. $C_{13}H_{24}O_2$ requires: C, 73·53; H, 11·39%); monobenzoate (IIIb), a colourless oil, b.p. 125–130°/0·8 mm, $[\alpha]_D^{24}$ −89·1° (±1·5°) (*c*, 1·680), $[M]_D$ −282°.

Condensation of IV with benzaldehyde. A solution of IV (50 mg) and benzaldehyde (50·4 mg) in EtOH (1 ml) and 10% NaOH (0·2 ml) was left over night at room temp and extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4), and evaporated leaving a residue (72·5 mg), which was recrystallized from acetone to give benzylidene compound V (62 mg) as colourless needles, m.p. 176–177°, ν_{max} 1716 and 1631 cm^{-1}, λ_{max} 295 mμ (ε 30,000). (Found: C, 80·72; H, 9·00. $C_{20}H_{26}O_2$ requires: C, 80·49; H, 8·78%.)

Trifluoroperacetic acid oxidation of IV. Trifluoroperacetic acid solution (trifluoroacetic anhydride, 2·68 g, and 80% H_2O_2, 0·45 g, in dichloromethane, 15 ml) was added dropwise to a stirred suspension of finely ground anhydrous sodium dibasic phosphate (2·3 g) in a solution of IV (223 mg) in dichloromethane (10 ml) during 10 min at 5–10°. The mixture was stirred for 18 hr at room temp, poured into water, and extracted with $CHCl_3$. The extract was washed with 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving the residue (246 mg), which was recrystallized from ether to give a δ-lactone (VI, 56·5 mg) and a mother liquor (190 mg). The mother liquor was hydrolysed with 5% KOH–MeOH to give VI (77·5 mg) as colourless needles (from ether), m.p. 114–115°, ν_{max} 1727 cm^{-1}, NMR 6·13 τ (triplet, J = 8·5 c/s). (Found: C, 68·96; H, 10·02. $C_{13}H_{22}O_3$ requires: C, 68·99; H, 9·80%.)

Conversion of the δ-lactone (VI) *into the keto-ester* (VIII). A solution of VI (112 mg) in 5% K_2CO_3–MeOH was refluxed for 1 hr and evaporated leaving a residue, which was dissolved in water (2 ml), neutralized with 2N acetic acid, and extracted with ether to give a hydroxy-acid (VII). This acid was dissolved in acetic acid (3 ml) and oxidized with a solution of CrO_3 (97 mg) in 95% acetic acid over night at room temp. The mixture was evaporated *in vacuo* and the residue was dissolved in water, acidified with 2N H_2SO_4, and extracted with ether. The ether extract was washed with $NaHCO_3$ solution and water, dried (Na_2SO_4), and evaporated leaving a lactonic fraction (56 mg). The aqueous layer was acidified with 2N H_2SO_4, extracted with ether, washed with water, dried (Na_2SO_4) and evaporated leaving a keto-acid (33 mg), which was treated with diazomethane to give VIII (34 mg), m.p. 52–64°, $\nu_{max}^{CCl_4}$ 1735 and 1716 cm^{-1}. As this keto ester (VIII) was partly dehydrated to give IX under treatment with neutral alumina in benzene, VIII was used for the following reaction without purification.

Dehydration of the keto-ester (VIII). A solution of VIII (33 mg) in 5% K_2CO_3–MeOH was refluxed for 1·5 hr and evaporated leaving a residue, which was dissolved in water and extracted with ether. The aqueous layer was acidified with 2N H_2SO_4 and extracted with ether. The extract was esterified with diazomethane to give IX (24 mg) as a colourless oil, b.p. 110–115°/0·6 mm, $[\alpha]_D^{27}$ +6·2° (±5°) (*c*, 0·390), λ_{max} 245 mμ (ε 10,200), ν_{max}^{film} 1737, 1670 and 1637 cm^{-1}. (Found: C, 70·35; H, 9·48. $C_{14}H_{22}O_3$ requires: C, 70·55; H, 9·31%.)

Lithium aluminium hydride reduction of oplopanone (I). A solution of I (1·0 g) in dry ether (30 ml) was added to a suspension of LAH (160 mg) in dry ether (30 ml) with stirring in an ice-bath and stirred for 30 min at room temp. To this mixture were added water and then 2N HCl, and the mixture was extracted with $CHCl_3$, washed with 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving a residue (1 g). The residue was recrystallized from ethyl acetate to give XVI (296 mg), colourless needles, m.p. 203–204°, $[\alpha]_D^{24}$ −7·9° (±4°) (*c*, 0·471). (Found: C, 74·87; H, 11·78. $C_{15}H_{28}O_2$ requires: C, 74·95; H, 11·74%) and an amorphous mixture (714 mg) of XVI and its epimer.

Dehydration of XVI *and its epimer.* A solution of a mixture (978 mg) of XVI and its epimer and methanesulphonyl chloride (700 mg) in pyridine (20 ml) was left overnight at room temp and refluxed for 3 hr. The mixture was evaporated *in vacuo*, extracted with ether, washed with 2N HCl and 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving a crystalline residue (840 mg), which was chromatographed on alumina to give a mixture (659 mg) of XVII and XVIII, the starting material (50 mg) and a hydrocarbon (a dehydration product of the tertiary hydroxyl group, 107 mg).

Osmium tetroxide oxidation of a mixture of XVII *and* XVIII. A solution of osmium tetroxide (885 mg) in dry dioxan (5 ml) was added to a solution of a mixture (659 mg) of XVII and XVIII in dry dioxan (25 ml) and left for 3 days at room temp. The mixture was saturated with H_2S and filtered. The filtrate was evaporated leaving a crystalline substance (667 mg), which was chromatographed on alumina to give XIXa (177 mg), colourless needles (from ethyl acetate), m.p. 202–204°, $[\alpha]_D^{24}$ −37·9° (±4°) (*c*, 0·572). (Found: C, 70·48; H, 11·03. $C_{15}H_{28}O_3$ requires: C, 70·27; H, 11·01%), XIXb (151 mg), colourless needles (from ethyl acetate), m.p. 173–175°, $[\alpha]_D^{24}$ −29·6° (±2°) (*c*, 0·891). (Found: C, 70·12; H, 11·08. $C_{15}H_{28}O_3$ requires: C, 70·27; H, 11·01%), and XX (33 mg), colourless plates (from acetone), m.p. 142·5–144°, $[\alpha]_D^{24}$ −12·2° (±3°) (*c*, 0·779). (Found: C, 70·48; H, 10·85. $C_{15}H_{28}O_3$ requires: C, 70·27; H, 11·01%.)

Oxidation of XIXa, XIXb *and* XX *with sodium periodate.* A solution of XIXa or XIXb (5 mg) and sodium periodate (8·3 mg) in MeOH (0·5 ml) and water (0·4 ml) was left overnight at room temp and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated leaving IV (4·2 mg or 4·4 mg, respectively). Compound XX (5 mg) was oxidized with sodium periodate under the same conditions to give XXI (4·5 mg), a colourless oil, ν_{max}^{film} 2730 and 1722 cm^{-1}.

Conversion of XIXa *into the ketone* (XXII). A solution of XIXa (167 mg) and methanesulphonyl chloride (155 mg) in pyridine (8 ml) was heated at 65–80° for 9 hr. The mixture was evaporated *in vacuo* and extracted with ether. The extract was washed with 2N H_2SO_4 and 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving a crystalline substance (157 mg), which was chromatographed on silica gel to give XXII, colourless needles (133 mg), m.p. 131·5–133·5° (from ether), $[\alpha]_D^{25}$ +7·0° (±5°) (*c*, 0·328), ν_{max} 1709 cm^{-1}. (Found: C, 75·58; H, 10·76. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 11·00%.) ORD of XXII: $[\alpha]_{700}$ −12°, $[\alpha]_{318}$ +2918°, $[\alpha]_{274}$ −3948°, $[\alpha]_{250}$ −2927° (*c*, 0·328; temp 25°).

Conversion of XIXb *into the ketone* (XXIII). A solution of XIXb (145 mg) and methanesulphonyl chloride (184 mg) in pyridine (7 ml) was heated at 80–85° for 13 hr. The mixture was evaporated *in vacuo* and extracted with ether. The extract was washed with 2N H_2SO_4 and 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving a crystalline substance (125 mg), which was chromatographed on silica gel to give the ketone (XXIII), colourless needles (57·2 mg), m.p. 109–110° (from light petroleum), $[\alpha]_D^{25}$ −58·1° (±4°) (*c*, 0·587), ν_{max} 1711 cm^{-1}. (Found: C, 75·95; H, 10·70. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 11·00%.) ORD of XXIII: $[\alpha]_{700}$ −34°, $[\alpha]_{315}$ +1608°, $[\alpha]_{272}$ −2688°, $[\alpha]_{250}$ −2368° (*c*, 0·587; temp 25°).

Conversion of XXII *into* XXIII. A solution of XXII (20·1 mg) in 10% NaOH (0·2 ml) and MeOH (2 ml) was left overnight at room temp and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated leaving a crystalline substance (18·3 mg), which was chromatographed on silica gel to give XXIII, m.p. 109–110° (13·5 mg).

Dehydrogenation[9] *of* XXII. Thionyl chloride (55 mg) was added to a solution of XXII (54·2 mg) in pyridine (1 ml) in an ice-bath and left for 30 min at room temp. The mixture was extracted with ether, washed with 2N H_2SO_4 and 2N Na_2CO_3, dried (Na_2SO_4), and evaporated leaving an oil (50·2 mg), which was chromatographed on alumina to give an oil (49·8 mg), ν_{max} 1708, 1648 and 895 cm^{-1}. A mixture of this oil (49·8 mg) and 10% Pd–C (25 mg) was heated at 310° for 1 min in a N_2 atmosphere and extracted with ether. The extract was further twice dehydrogenated under the same manner. The ether extract, a pale yellow oil (42·2 mg) afforded a colourless oil (XXIV; 27·2 mg); trinitrobenzene adduct, vermilion needles, m.p. 132–134° (from EtOH). (Found: C, 59·50; H, 4·66; N, 10·13. $C_{21}H_{21}O_7N_3$ requires: C, 59·01; H, 4·95; N, 9·83%) by preparative TLC. Compound XXIV was shown to be identical with 8-isopropyl-2,5-dimethyl-1-naphthol by comparison of IR spectra and by mixed m.p. determination of trinitrobenzene adducts.

Acknowledgement—The authors are very much indebted to Prof. S. Okura (Shinshu University) for the collection of the plant.

[9] H. Minato, M. Ishikawa and T. Nagasaki, *Chem. Pharm. Bull. Tokyo* **13**, 717 (1965).