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REVISIONS OF THE ABSOLUTE CONFIGURATIONS OF C-8 METHYL GROUPS IN DEHYDROIRIDODIOL, NEONEPETALACTONE, AND MATATABIETHER FROM *ACTINIDIA POLYGAMA* MIQ

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Abstract—The absolute configurations of C-8 Me groups in dehydro-iridodiol, neonepetalactone, and matatabiether isolated from the cat- and lacewing-attracting plant *Actinidia polygama* Miq. were revised to the *S* configurations on the basis of chemical transformations and unambiguous syntheses.

The preceding paper[1] reported the isolation and structural determination of the pungent principle, which was designated as dehydroiridodial and assigned formula **1** with the 3*R*,8*S*[2] configuration, from fresh fruits of the cat- and lacewing-attracting plant *Actinidia polygama* Miq. Recently, we discovered that the spectral data of dehydroiridodiol (**2**) derived from **1** by LAH reduction resembled those[3] of natural dehydroiridodiol, which had been assigned the (3*R*,8*R*)-configuration (**2'**).[4]

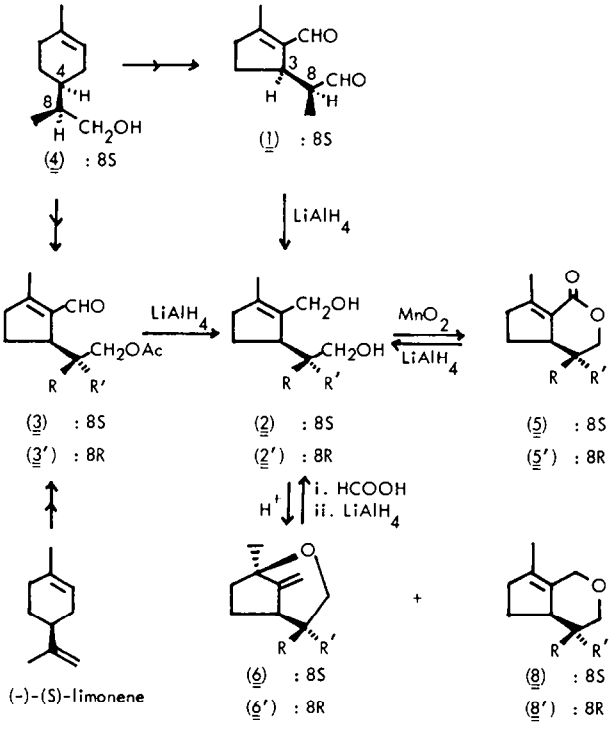
To resolve this unexpected discrepancy,[5] we attempted to synthesize two unambiguous diastereoisomeric dehydroiridodiols (**2** and **2'**) from (−)-(*S*)-limonene by modifications of the procedures for synthesis of dehydroiridodial.[1,6] The mixture of diastereoisomeric acetate aldehydes (**3** and **3'**) could be separated into the individual isomers **3** ($[\alpha]_D^{28}$ + 23.1°) and **3'** ($[\alpha]_D^{28}$ + 7.3°) by means of preparative gas chromatography. The stereochemistry of these isomers were unequivocally established as the (3*R*,8*S*)-acetate aldehyde for **3** and the (3*R*,8*R*)-isomer for **3'**, because the former was separately prepared from (−)-(4*S*,8*S*)-*p*-menth-1-en-9-ol (**4**)[7] in the same way. Thus, the (3*R*,8*S*)-diol **2** ($[\alpha]_D^{28}$ − 20.7°) and the (3*R*,8*R*)-diol **2'** ($[\alpha]_D^{28}$ − 15.3°) were obtained from the corresponding acetate aldehydes **3** and **3'** by LAH reduction, respectively. The IR and NMR spectra and optical rotations of natural dehydroiridodiol and the diol derived from natural dehydroiridodial (**1**) by LAH reduction were identical to those of the synthesized (3*R*,8*S*)-diol **2**, but not of the (3*R*,8*R*)-diol **2'**.

As the stereochemistry of dehydroiridodiol, neonepetalactone,[8] and matatabiether[9] had been deduced to be of the (3*R*,8*R*)-configuration (**2'**, **5'** and **6'**, respectively) on the basis of the chemical transformation of neonepetalactone into isodihydronepetalactone (**7'**) with the well-established structure, we reinvestigated their correlations. According to the procedures previously reported,[9] the synthesized (3*R*,8*S*)-diol **2** was treated with acid to give the ethers **6** and **8**.[10] The ether **6** was identical with natural matatabiether. Subsequently, this ether **6** was returned to the (3*R*,8*S*)-diol **2** by treatment with formic acid followed by LAH reduction. Furthermore, LAH reduction of naturally occurring neonepetalactone gave the (3*R*,8*S*)-diol **2**, and MnO_2 oxidation of this diol regenerated the lactone **5**, which was identical with natural neonepetalactone. Consequently, the absolute configurations of dehydroiridodiol, neonepetalactone, and matatabiether at C-8 have to be revised to the *S* configurations from the previously deduced *R* ones.

The erroneous original assignment[4] of the C-8 Me configuration (*R*) of the compounds under consideration was based upon the fact that hydrogenation of neonepetalactone with Adams catalyst in ether gave a mixture of two saturated lactones, and the major lactone was characterized as isodihydronepetalactone (**7'**) by means of only IR and NMR spectra, without ORD and $[\alpha]_D$ data. On comparison of ORD spectra and $[\alpha]_D$ of the major lactone with those of the natural lactone **7'**, we now found that the major hydrogenated product was not isodihydronepetalactone itself, but its enantiomer **9**. That is, the ORD spectrum of the natural lactone **7'** showed a negative Cotton effect ($[\phi]_{231}$ − 2987), whereas that of the hydrogenated product **9** exhibited a positive one ($[\phi]_{231}$ + 3054). The enantiomeric relation between **7'** and **9** was further confirmed by LAH reduction into their corresponding enantiomeric alcohols **11'** and **10** one of which, α-iridodiol (**11'**), had a known absolute configuration.[10] The minor hydrogenated product was established as being 1-epi-dihydronepetalactone (**12**) by means of spectral analysis. The IR spectrum of **12** was similar to that of dihydronepetalactone (**7**)[4] and the NMR spectrum of **12** closely resembled that of **7**, except for the signals of the C-1 Me protons: the (1*R*)-Me signals of **12** appeared at about 0.20 ppm higher field than the (1*S*)-Me signals of **7**.

On the catalytic hydrogenation of neonepetalactone with PtO_2 in ether, the formation of the unexpected enantiomer **9** of isodihydronepetalactone (**7'**) and 1-epi-dihydronepetalactone (**12**), became clear by the

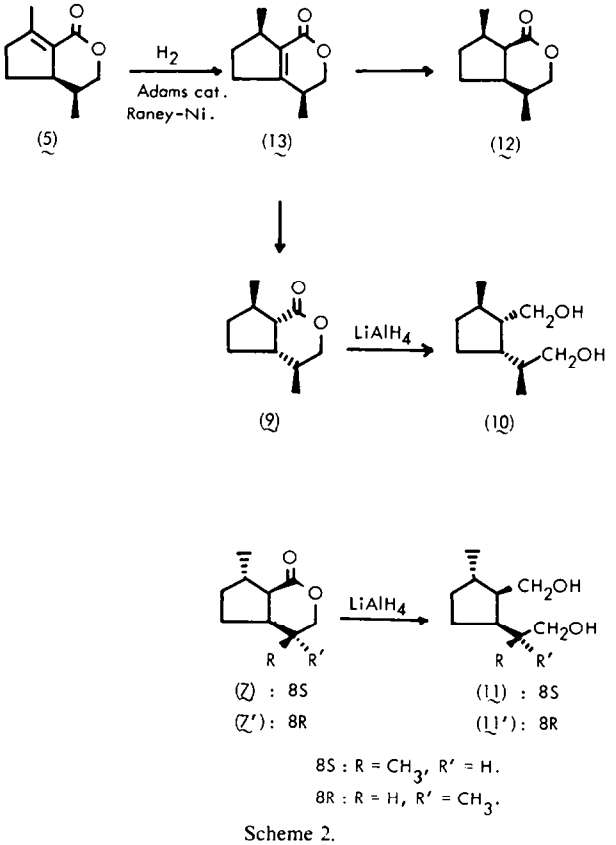
**The previous name. The Institute of Food Chemistry.



8S : R = CH_3, R' = H.

8R : R = H, R' = CH_3.

Scheme 1.



8S : R = CH_3, R' = H.

8R : R = H, R' = CH_3.

Scheme 2.

isolation of intermediate **13**, which was characterized on the basis of spectral data; IR: 1720, 1645 cm^{-1} (α,β-unsaturated δ-lactone); NMR: δ 1.10, 1.20 (each 3 H, d, J = 7 Hz; two secondary Me groups). The C-1 Me configuration (*R*) was supported by the well-known stereochemistry of allylic hydrogen migration on the catalytic hydrogenation[11] and further results of a more detailed hydrogenation.

By checking compositions of the hydrogenation products with gas chromatography at regular time intervals, we found that the migration of the double bond was completed in 45 min with Adams catalyst and in 20 min with Raney nickel, as shown in Fig. 1. The process with Adams catalyst may be interpreted as follows: first, migration of the double bond at C-1 and C-2 to C-2 and C-3 occurred, then the reduction took place with the more stable lactone **9** as the main product, presumably due to the thermodynamically controlled addition of hydrogen. The less stable *cis,cis*-lactone **12** was the minor reduction product, although it might have been expected from the addition of hydrogen from the less-hindered side of the intermediate molecule **13**. Indeed, hydrogenation of neonepetalactone (**5**) with Raney nickel in ethanol afforded a mixture of **9** and **12** in the expected ratio of 1:6.

On the basis of these results, the other compounds isolated from this plant with structures determined in correlation to dehydroiridodiol and metatabiether must be also revised from the 8*R* to the 8*S* configuration. Correction of the previous assignment will be discussed in a forthcoming publication.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard on a JEOL JNM-FX100 instrument. IR spectra were taken as thin films between NaCl plates on a Hitachi EPI-G2 spectrometer equipped with a beam condenser. Optical rotations were measured in $CHCl_3$ on a Perkin–Elmer Model 141 polarimeter. ORD and CD curves were recorded in EtOH on a JASCO J-20C instrument. Mass spectra were obtained on a Hitachi RMU-6 mass spectrometer (for GC-MS) or a JEOL JMS-01SG (for high resolution mass spectra) instrument. Glc was performed on a Hitachi 163 (for analytical work) or a Varian aerograph 920 (for preparative work) instrument, using a 45 m × 0.25 mm glass capillary column coated with PEG 20M or Thermon 600T (analytical and GC-MS) or a 3 m × 10 mm aluminium column packed with 5% Thermon 1000 on Chromosorb W (preparative).

Isolation of dehydroiridodial, neonepetalactone and matatabiether. Fresh fruits (7 kg, collected in Toyama Pref. in August 1978) were steam distilled and the essential oil (5.8 g) was chromatographed over silicic acid. Elution with benzene/EtOAc (5:1) gave **1** (2.0 g). Elution with benzene/EtOAc (1:1) gave a mixture of **5** and an unknown lactone (940 mg). Preparative Glc yielded pure samples of each lactone (*ca* 10:1). Air-dried fruits (1.3 kg) were steam distilled to obtain the essential oil (330 mg) from which **6** (60 mg) was isolated by preparative Glc.

Dehydroiridodial (**1**); $[\alpha]_D^{23}$ + 80.0° (*c* = 1.00); UV: λ_{max}^{EtOH} 253 nm, log ε 4.08; IR: 2740, 1725, 1660 cm^{-1}; NMR: δ 1.01 (3 H, d, J = 7 Hz, C-8 Me), 2.17 (3 H, s, C-1 Me), 9.96 (1 H, d, J = 1 Hz, C-8 CHO), 10.02 (1 H, s, C-2 CHO); MS: 166 (12%, M$^+$), 148 (17), 138 (23), 123 (12), 109 (66), 108 (47), 95 (16), 81 (100), 79 (30), 67 (21), 53 (15) and 41 (22); [Found, M$^+$ 166.0996. $C_{10}H_{14}O_2$ requires: M$^+$ 166.0993].

Neonepetalactone (**5**); $[\alpha]_D^{23}$ − 166.8° (*c* = 0.31). UV: λ_{max}^{EtOH} 239 nm, log ε 4.01. IR: 1710, 1638 cm^{-1}; NMR: δ 0.97 (3 H, d, J = 7 Hz, C-8 Me), 2.23 (3 H, t, J = 1 Hz, C-1 Me), 3.19 (1 H, m, C-3 H), 4.19, 4.34 (each 1 H, AB q of ABX, J_{AX} = 3 Hz, J_{BX} = 3 Hz, J_{AB} = 11 Hz, C-9 H_2); MS: 166 (100%, M$^+$), 151 (26), 148 (23), 136 (15), 133 (7), 124 (91), 109 (14), 108 (24), 107 (32), 105 (15), 93 (62), 91 (30), 81 (22), 80 (38), 79 (90), 77 (33), 69 (10), 67 (15), 65 (15), 58 (13), 55 (12), 53 (16), 51 (16), 43 (16), 41 (22) and 39 (24); [Found, M$^+$ 166.0993. $C_{10}H_{14}O_2$ requires: M$^+$ 166.0993]. The IR and NMR spectra of **5** were identical to those of the authentic sample.

Matatabiether (**6**); $[\alpha]_D^{23}$ − 147.3° (*c* = 1.03); IR: 3100, 1675, 1085, 1045, 890 cm^{-1}; NMR: δ 0.77 (3 H, d, J = 7 Hz, C-8 Me), 1.32 (3 H, s, C-1 Me), 3.40, 3.66 (each 1 H, AB q of ABX, J_{AX} = 12 Hz, J_{BX} = 6 Hz, J_{AB} = 12 Hz, C-9 H_2), 4.74 (2 H, s, C-7 H_2); MS: 152 (39%, M$^+$), 137 (44), 124 (17), 110 (47), 109 (34), 95 (100), 81 (28), 67 (35), 55 (20) and 43 (54); [Found, M$^+$ 152.1193. $C_{10}H_{16}O$ requires: M$^+$ 152.1198].

Synthesis of dehydroiridodiols (**2** and **2′**)

(4S,8R/S-p-Menth-1-en-9-yl acetates. Hydroboration of (−)-(*S*)-limonene ($[\alpha]_D^{20}$ − 93.5°) with disiamylborane according to the method of Pawson *et al.*[7] afforded a mixture of the diastereoisomeric alcohols (**4** and its 8*R*-isomer; $[\alpha]_D^{26}$ − 96.7°, *c* = 0.39) in 43% yield. This mixture was acetylated in the usual manner (Ac_2O/pyridine) to afford a mixture of (4*S*,8*S*)- and (4*S*,8*R*)-acetates (yield 96%) in a ratio of 1:1, according to NMR. This acetate mixture showed $[\alpha]_D^{26}$ − 71.4° (*c* = 1.09). IR: 1730, 1230 cm^{-1}; NMR: δ 0.91, 0.93 (combined 3 H, each d, J = 7 Hz, C-8 Me), 1.63 (3 H, br s, C-1 Me), 2.03 (3 H, s, OAc), 5.34 (1 H, br s, C-2H); MS: 196 (2%, M$^+$), 136 (28), 121 (27), 107 (23), 95 (25), 94 (100), 93 (42), 79 (28), 68 (17), 55 (9), 43 (30) and 41 (10).

(3R,8S)- and (3R,8R)-1-Methyl-2-formyl-3(β-acetoxyisopropyl)cyclopentenes (**3** *and* **3′**). According to our preceding paper[1] or the procedure of Meinwald and Jones,[6] a soln containing all of the crude products from ozonolysis (MeOH, −70°/1 hr) of 8.0 g of the acetate mixture, 5 ml piperidine, and 5 ml AcOH in 100 ml dry benzene was refluxed using a Dean Stark trap for 5 hr. After the usual work up, the resulting brown oily material was chromatographed on silicic acid. Elution with benzene–EtOAc (10:1) gave the unreacted starting material (0.41 g) and the desired acetate aldehyde mixture (**3** and **3′**; 1.63 g). Glc and NMR analysis of this mixture indicated that it was composed of 73% of **3** and 27% of **3′**. Pure **3** and **3′** were separated by preparative Glc. The major isomer **3**, with shorter retention time in Glc, showed $[\alpha]_D^{27}$ + 23.1° (*c* = 0.16); NMR: δ 0.95 (3 H, d, J = 7 Hz, C-8 Me), 2.00 (3 H, s, OAc), 2.14 (3 H, t, J = 1 Hz, C-1 Me), 3.83, 3.88 (2 H, AB q, J_{AB} = 7 Hz, C-9 H_2), 10.00 (1 H, s, C-2 CHO); MS: 210 (1%, M$^+$), 168 (6), 150 (100), 135 (33), 121 (17), 109 (72), 107 (31), 93 (13), 91 (11), 81 (85), 79 (29), 77 (12), 67 (6), 65 (4), 53 (9), 43 (49) and 41 (15). This isomer was identified in all respects as (3*R*,8*S*)-1-methyl-2-formyl-3(β-acetoxyisopropyl) cyclopentene, which was derived from **4** of the known absolute configuration ($[\alpha]_D^{23}$ − 102.2°, lit.[7] $[\alpha]_D^{25}$ − 103.1°), by the procedure described above. The minor 3*R*,8*R* isomer **3′** showed $[\alpha]_D^{27}$ + 16.8° (*c* = 0.56); IR: the same as **3**; NMR: δ 0.69 (3 H, d, J = 7 Hz, C-8 Me), 2.04 (3 H, s, OAc), 2.15 (3 H, t, J = 1 Hz, C-1 Me), 3.92 (2 H, d, J = 7 Hz, C-9 H_2), 9.99 (1 H, s, C-2 CHO); MS: 210 (4%, M$^+$), 168 (5), 150 (100), 135 (52), 121 (22), 109 (87), 107 (47), 93 (22), 91 (17), 81 (89), 79 (37), 67 (9), 65 (10), 53 (14) and 43 (83).

Dehydroiridodiol **2** *and isodehydroiridodiol* **2′**. A soln of **3** or **3′** (97 mg) in dry ether (2 ml) was added to a stirred and ice-cooled suspension of LAH (20 mg) in dry ether (3 ml). The mixture was stirred for 30 min at room temp. The excess LAH was destroyed by careful addition of water and the white ppt was filtered off. The ether soln was dried and the solvent was evaporated. Purification of the residue by column chromatography on silicic acid gave the diols **2** or **2′** in *ca* 50% yield.

The (3*R*,8*S*)-diol **2** (dehydroiridodiol) derived from **3** showed $[\alpha]_D^{27}$ − 20.7° (*c* = 2.28); IR: 3300, 1645, 1020, 1000 cm^{-1}; NMR: δ 0.89 (3 H, d, J = 7 Hz, C-8 Me), 1.70 (3 H, t, J = 1 Hz, C-1 Me), 2.86 (2 H, br s, 2 × OH), 3.43, 3.51

(each 1 H, AB q of ABX, J_{AX} = 8 Hz, J_{BX} = 6 Hz, J_{AB} = 11 Hz, C-9 H_2), 4.17 (2 H, s, C-7 H_2); MS: 152 (27%, M$^+$ − 18), 137 (49), 122 (53), 107 (100), 105 (31), 93 (45), 91 (59), 79 (58), 77 (33), 65 (17), 53 (16) and 41 (33).

The (3*R*-8*R*)-diol **2'** (isodehydroiridodiol) derived from **3'** showed $[\alpha]_D^{27}$ − 15.3° (*c* = 0.78); IR: 3300, 1645, 1020, 1000 cm^{-1}; NMR: δ 0.67 (3 H, d, J = 7 Hz, C-8 Me), 1.70 (3 H, t, J = 1 Hz, C-1 Me), 2.88 (1 H, br s, OH), 3.10 (1 H, br s, OH), 3.45, 3.47 (each 1 H, AB q of ABX, J_{AX} = 8 Hz, J_{BX} = 6 Hz, J_{AB} = 11 Hz, C-9 H_2), 4.01, 4.25 (each 1 H, AB q, J_{AB} = 12 Hz, C-7 H_2); MS: 152 (27%, M$^+$ − 18), 137 (100), 122 (36), 107 (77), 95 (44), 93 (33), 91 (45), 79 (58), 67 (26), 55 (20), 53 (18) and 41 (36).

The IR and NMR spectra and $[\alpha]_D$ of dehydroiridodiol derived from natural dehydroiridodial by LAH reduction were identical to those of the synthesized 3*R*,8*S*-diol **2**.

Interconversion of matatabiether or neonepetalactone and dehydroiridodiol

Conversion of dehydroiridodiol (**2**) *into matatabiether* (**6**). A mixture of 330 mg of the synthesized diol **2** in 2 ml of CCl_4 and 235 mg of I_2 was stirred for 5 min at room temp. The mixture was washed with sat Na_2SO_3 aq, sat $NaHCO_3$ aq and water. Evaporation of the solvent gave a mixture of the ethers. Glc analysis indicated that the mixture contained **6** and **8** in a 1:4 ratio. Pure **6** was isolated by preparative Glc. The IR and NMR spectra and $[\alpha]_D$ of **6** were identical to those of natural matatabiether.

Conversion of **6** *into* **2**. A mixture of **6** (3.0 g) and 85% HCOOH (20 ml) was stirred for 6 hr at room temp. The mixture was poured into ice water, neutralized with 5% $NaHCO_3$ aq and extracted with ether. Distillation of the ether extract gave 509 mg (yield 11%) of diformate; bp. 110–120°/5 mm; NMR: δ 0.99 (3 H, d, J = 6 Hz, C-8 Me), 1.73 (3 H, s, C-1 Me), 3.74, 4.11 (each 1 H, AB q of ABX, J_{AX} = 11 Hz, J_{BX} = 6 Hz, J_{AB} = 11 Hz, C-9 H_2), 4.73 (2 H, s, C-7 H_2), 8.00, 8.03 (each 1 H, s, 2 × CHO).

A soln of the diformate (500 mg) in 5 ml of dry ether was added to a suspension of LAH (300 mg) in dry ether (10 ml). The mixture was refluxed for 3 hr. After the usual work up, the residue was chromatographed on alumina. Elution with MeOH afforded 334 mg of pure **2**. Its IR and NMR spectra agreed with those of the synthesized diol **2**.

Conversion of dehydroiridodiol (**2**) *into neonepetalactone* (**5**). A mixture of 220 mg of the synthesized diol **2**, 5.0 g of MnO_2, and 15 ml of $CHCl_3$ was stirred for 30 hr at room temp. After the usual work up, the residue was refluxed with a soln of 200 mg of NaOH in 2 ml of water for 30 min. The alkaline soln was acidified with 4N HCl and extracted with ether. Evaporation of the solvent afforded 57 mg of crude lactone. Distillation gave 35 mg (yield 16%) of pure **5**, with IR and NMR spectra agreeing with those of natural neonepetalactone.

Conversion of **5** *into* **2**. LAH reduction of natural lactone **5** gave the unsaturated diol **2** in 90% yield. The NMR spectrum of this diol was identical to that of the synthesized diol **2**.

Catalytic hydrogenation of neonepetalactone (**5**)

General procedure. In order to monitor the reaction progress, a mixture of 20 mg of the lactone **5** in 3 ml of solvent (ether or ethanol) and 10 mg of catalyst (PtO_2 or Raney Ni) was stirred under a hydrogen pressure of 1 atm at room temp. At regular intervals, the mixture was examined by analytical Glc. The composition of the mixture was determined by Glc peak areas. To isolate the reduction products, a mixture of 100 mg of **5**, 3 ml of solvent, and 25 mg of catalyst was stirred until the amount of the desired component reached a maximum. Filtration of the catalyst and evaporation of the solvent gave a mixture of the reduction products. The mixture was separated by preparative Glc.

The enantiomeric isodihydronepetalactone (**9**). The lactone **5** was hydrogenated in ether over PtO_2 for 3 hr. Glc analysis indicated the presence of two reduction products **9** (95%) and **12** (5%). A pure sample of the major lactone **9**, isolated by prepative Glc, showed $[\alpha]_D^{28}$ − 1.20° (*c* = 1.33); ORD: $[\phi]_{231}$ + 3054; IR: 1735 cm^{-1}; NMR: δ 0.97 (3 H, d, J = 7 Hz, C-8 Me), 1.18 (3 H, d, J = 7 Hz, C-1 Me), 3.87, 4.12 (each 1 H, AB q of ABX, J_{AX} = 9 Hz, J_{BX} = 4 Hz, J_{AB} = 11 Hz, C-9 H_2); MS: 168 (16%, M$^+$), 153 (57), 139 (12), 126 (21), 123 (18), 113 (100), 100 (6), 95 (36), 81 (79), 69 (36), 67 (53), 55 (21) and 41 (37). This lactone was identical in all respects (IR, NMR, and mass), except for $[\alpha]_D$ and ORD, to natural isodihydronepetalactone ($[\phi]_{231}$ − 2987).

1-*Epi-dihydronepetalactone* (**12**). The lactone **5** was hydrogenated in EtOH over Raney Ni for 4 hr. The product was analyzed by Glc; 80% of **12**, 13% of **9**, and 7% of **13**. The major saturated lactone **12** was separated by preparative Glc and showed $[\alpha]_D^{28}$ − 17.9° (*c* = 0.80); IR: 1730 cm^{-1}; NMR: δ 0.92 (3 H, d, J = 7 Hz, C-8 Me), 0.99 (3 H, d, J = 7 Hz, C-1 Me), 4.02 (1 H, d, J = 8 Hz, C-9H), 4.03 (1 H, d, J = 9 Hz, C-9 H); MS: 168 (6%, M$^+$), 153 (2), 139 (6), 126 (19), 113 (100), 108 (10), 107 (6), 95 (27), 81 (35), 69 (18), 67 (33), 55 (15) and 41 (26).

The hydrogenation intermediate **13**. The lactone **5** was hydrogenated in ether over PtO_2 for 40 min. The mixture contained 88% of **13** and 12% of **9**. The major unsaturated lactone **13** was isolated by preparative Glc and showed $[\alpha]_D^{24}$ − 8.6° (*c* = 1.75); IR: 1720, 1640 cm^{-1}; NMR: δ 1.11 (3 H, d, J = 7 Hz, C-8 Me), 1.20 (3 H, d, J = 7 Hz, C-1 Me), 3.96, 4.35 (each 1 H, AB q of ABX, J_{AX} = 9 Hz, J_{BX} = 5 Hz, J_{AB} = 11 Hz, C-9 H_2); MS: 166 (100%, M$^+$), 151 (51), 136 (39), 123 (27), 121 (53), 113 (19), 109 (35), 107 (43), 95 (67), 93 (37), 91 (30), 81 (57), 79 (36), 77 (25), 67 (47), 55 (24), 43 (32), 41 (37) and 39 (24).

LAH reduction of the enantiomeric isodihydronepetalactone. The lactone **9** (70 mg) in dry ether (4 ml) was added dropwise to a suspension of LAH (100 mg) in dry ether (8 ml). The mixture was refluxed for 2 hr. After the usual work up, the residual crystalline solid was recrystallized from hexane/$CHCl_3$ to give 59 mg of the diol **10**; mp 76–79°; $[\alpha]_D^{28}$ − 4.81° (*c* = 0.81). The IR and NMR spectra were identical to those of α-iridodiol (**11**: mp 76–79°, $[\alpha]_D^{28}$ + 6.46°, *c* = 4.13) derived from natural isodihydronepetalactone.

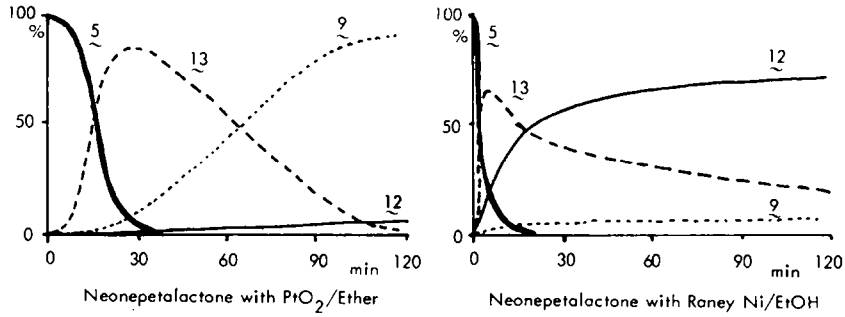


Fig. 1. Time-course observation of hydrogenation products. **5**: Neonepetalactone; **13**: The migration product; **9**: The enantiomer of isodihydronepetalactone; **12**: 1-Epi-dihydronepetalactone.

Acknowledgement—We are indebted to Prof. F. Murai, Aichi Medical University, for his valuable suggestions.

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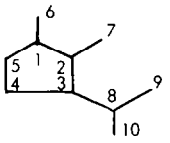

[3]Unpublished data; $[\alpha]_D^{20}$ − 16.7 (c = 1.00); IR: 3320, 1030 cm^{-1}; NMR (60 MHz, in CCl_4): δ 0.90 (3 H, d, J = 7 Hz), 1.75 (3 H, s), 3.6 (2 H, m), 4.27 (2 H, s), 4.65 (2 H, s). cf. T. Maeda, M.D Thesis, Osaka City University (1967).

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[5]The C-8 chiral center of dehydroiridodial (**1**) is labile, since pure (3*R*,8*S*)-dial changed into a mixture of **1** and its (3*R*-8*R*)-isomer (*ca* 1:1 ratio) on preparative Glc. Therefore, dehydroiridodiol (**2**) obtained from **1** by LAH reduction seemed to be suspicious of the configuration at C-8.

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[9]S. Isoe, T. Ono, S. B. Hyeon and T. Sakan, *Ibid.* 5319 (1968).

[10]This compound has been assigned as **8′** with (3*R*,8*R*)-configuration in Lit 9.

[11]cf. H. J. Brodee, M. Hayano and M. Gut, *J. Am. Chem. Soc.* **84**, 3766 (1962).