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SESQUITERPENES OF *LAURACEAE* PLANTS—III[1]
STRUCTURE AND ABSOLUTE CONFIGURATION OF DELOBANONE AND ACETOXYDELOBANONE FROM *LINDERA TRILOBA*

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Abstract—Two new sesquiterpenes, delobanone and acetoxydelobanone, have been isolated from the root of *Lindera triloba* and characterized as 4-oxo-α-bisabolol (I) and its 1α-acetoxy derivative (II), respectively. NMR studies on an O-benzylidene derivative of 1α-hydroxydelobanone (V) clarified the stereochemistry at C-7 of these sesquiterpenoids.

IN CONTINUATION of our chemical studies on *Lauraceae* plants, we have examined the sesquiterpenic constituents of *Lindera triloba* Sieb, et Zucc. Blume (Japanese name "shiromoji"). A neutral ether extract of the root of this plant was submitted to repeated chromatography to yield two new sesquiterpenes of the bisabolane type, for which we propose the names delobanone (I, 0·14% yield) and acetoxydelobanone (II, 0·09%), respectively.

Delobanone (I) is a colorless oil, $C_{15}H_{24}O_2$ (M^+ 236), $[\alpha]_D$ + 10·2°, and exhibits absorptions typical for a OH group (ν_{max} 3600 and 3500 cm^{-1}) and an αβ-unsaturated ketone system [λ_{max} 237 mμ (ε 8600) and ν_{max} 1680 cm^{-1}]. On hydrogenation over Pd-C delobanone absorbed two moles of hydrogen to give a saturated tetrahydro derivative (III), a colorless oil, $[\alpha]_D$ − 15·1°, showing an absorption at 1714 cm^{-1} (six-membered ring ketone) together with a band at 3500 cm^{-1} (OH). This spectral and chemical evidence showed that delobanone (I) is a monocyclic sesquiterpene having one double bond besides one OH group and the αβ-unsaturated ketone system. The NMR spectrum of delobanone (I) in C_6D_6 revealed the presence of a tertiary Me group on the carbon carrying the OH group (τ 9·15, 3H, s; this signal shifts to 8·87 in CCl_4), three Me groups on two double bonds (τ 8·45, 3H, d, J = 2 Hz; 8·33, 3H, d, J = 2 Hz and 8·20, 3H, d, J = 2 Hz), and two olefinic protons (τ 4·87, 1H, broad t and 3·80, 1H, m). One of the olefinic protons should be located at a position β to the conjugated carbonyl group on the basis of its chemical shift (τ 3·80), so that a $-CH{=}C(CH_3)-\underset{|}{C}{=}O$ grouping must be present in the six-membered ring of delobanone (I). The other olefinic proton and two Me groups should form a $(CH_3)_2C{=}CH-CH_2-$ grouping, because the signal pattern of the olefinic proton at τ 4·87 shows the presence of two hydrogen atoms on the adjacent carbon atom. This is also supported by presence of a very strong peak at *m/e* 69 (88%)[2] in the mass spectrum of delobanone (I), the peak being ascribable to the isopentenyl group. Combination of these partial structures and biogenetical considerations led to the structure 4-oxo-α-bisabolol (I) for delobanone.

This assignment was confirmed by conversion of delobanone (I) into the enantiomer of cryptomerion, whose structure is known.[3] Treatment of I with $SOCl_2$ in pyridine

gave a mixture of two dehydrated products, from which the main product (IV) was separated by prep GLC. This compound (IV) showed IR and NMR spectra superimposable with those of cryptomerion[3] and exhibited optical activity of opposite sign to that of cryptomerion.[3]

Another sesquiterpene constituent of this plant, acetoxydelobanone (II), a colorless oil, $C_{17}H_{26}O_4$ (M^+ 294), $[\alpha]_D$ + 207°, was considered to have the same structure as delobanone (I) with an additional secondary OAc group from its spectral evidence: ν_{max} 3600, 3525 (OH), 1742, 1227, 1214 (OAc), and 1688 cm^{-1} and

λ_{max} 229·5 mμ (ε 9700) (αβ-unsaturated ketone); τ (CCl_4) 8·80 (3H, s) [HO—C—$C\underline{H}_3$],

8·40 (3H, d, J = 1·5 Hz), 8·33 (3H, d, J = 1·5 Hz) and 4·93 (1H, broad t) [—CH_2—$C\underline{H}$=$C(C\underline{H}_3)_2$], 8·23 (3H, d, J = 1·5 Hz) and 3·28 (1H, d-d, J = 1·5 and 6 Hz)

[—CH—$C\underline{H}$=$C(C\underline{H}_3)$—C=O], 7·95 (3H, s) [OAc], and 4·75 (1H, d-d, J = 3 and 6 Hz)

[—CH—$C\underline{H}$(OAc)—CH].

The presence of a secondary OAc group was also shown by the fact that saponification of acetoxydelobanone (II) gave hydroxydelobanone (V), $C_{15}H_{24}O_3$, m.p. 97–98°, which easily regenerated acetoxydelobanone (II) on acetylation under mild conditions. On hydrogenation over Pd-C, hydroxydelobanone (V) absorbed two moles of hydrogen to give a tetrahydro derivative (VI), m.p. 92–93°, the IR spectrum of which showed the presence of a six-membered ring ketone (ν_{max} 1710 cm^{-1}) in its molecule. The location of the OAc group in II was assigned at C-1 by the fact that CrO_3 oxidation of hydroxydelobanone (V) afforded an oily product (VII), whose spectroscopic properties [λ_{max} 253·9 mμ (ε 15,000); ν_{max} 1657 cm^{-1}; τ 8·40 (3H, d, J = 1·8 Hz), 3·95 (1H, q, J = 1·8 Hz) and 3·20 (1H, s)] showed it to contain a *p*-quinone system[4,5] in the molecule.

Successful interconversion of acetoxydelobanone (II) with delobanone (I) confirmed this assignment. Reduction of acetoxydelobanone (II) with Ca in liquid NH_3 resulted in hydrogenolytic removal of the allylic OAc group[6] and partial hydrogenation of the conjugated double bond[7] to give an oily mixture with an absorption band at 1710 cm^{-1}. Hydrogenation of this mixture over Pd-C gave a single saturated ketone, which was identified with tetrahydrodelobanone (III) by comparison of their IR spectra and $[\alpha]_D$ values, and by m.m.p. determination of their 2,4-dinitrophenylhydrazones.

The absolute configuration of acetoxydelobanone (II) was established as follows. The ORD curves of the saturated ketones (III and VI) showed negative Cotton effects (a = −53 and −32, respectively). Since the bulky C-6 side chain must have an equatorial conformation, the sign of the Cotton effect showed that the configuration of the side chain is α in both compounds (III and VI). The same equatorial conformation of the side chain in 1-hydroxydelobanone (V) as in VI was shown by the double resonance NMR data of the compound (V); the coupling constant (13 Hz) between H-6 and H-5_{ax} suggests the dihedral angle of these protons to be about 180°, i.e. H-6 has axial conformation. Further, the coupling constant (3 Hz) between H-6 and H-1 shows that the dihedral angle of the two protons is about 60°, i.e. H-1 is in a β-equatorial conformation. Thus the OH group at C-1 in V has an α-axial orientation.

(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
H2/Pd-C
SOCl2/py
1) Ca/NH3
2) H2/Pd-C
OH⊖
CrO3
H2/Pd-C
CHO

CHART 1

To study the stereochemistry at C-7, it is necessary to prohibit the rotation around this carbon atom. It is well known in carbohydrate chemistry that two OH groups on alternate carbon atoms react with benzaldehyde to give a six-membered cyclic O-benzylidene compound, in which the Ph group stands in the less-hindered equatorial conformation.[8] Treatment of the diol (V) with benzaldehyde afforded an O-benzylidene compound (VIII), m.p. 98–99°. As no notable changes were observed in the signal pattern of H-1 in its NMR spectrum, the benzylidene compound (VIII) proved to retain the same conformation at C-1 and C-6 as the starting diol (V). Thus, alternative structures (VIIIa and VIIIb) are suggested for the α- and β-configurations of the OH group at C-7 (Fig. 1). Intramolecular nuclear Overhauser effect (NOE)[9] should be observed between H-1 and H-15, H-1 and H-16, and H-15 and H-16 respectively in VIIIa, whereas in VIIIb the effect would not be observed between H-1 and H-15, and H-15 and H-16. Table 1 summarizes the results of the NOE measurement, which prefer the conformer VIIIa to VIIIb.

TABLE 1. NOE VALUES (INCREASES IN INTEGRATED INTENSITIES, %)[a] FOR (VIII) IN C_6D_6

	1-H	15-H	16-H
τ	5·88 d-d	8·90 s	4·33 s
NOE	20 [15-H]	+ [1-H]	9 [1-H]
	11 [16-H]	+ [16-H]	20 [15-H]

[a] Saturated signals are shown in brackets.

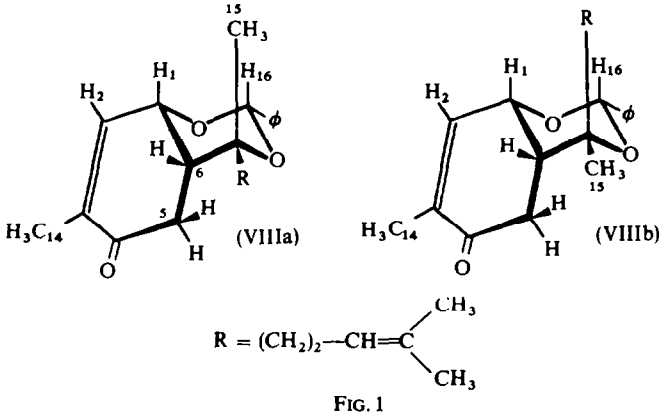

FIG. 1

The absolute configurations (I) and (II) were therefore assigned to delobanone and acetoxydelobanone, respectively.

These results also established the stereochemistry of cryptomerion, which was not given by Nagahama,[3] to be the mirror image of structure IV, since one of the dehydrated compounds of delobanone was found to be the antipode of cryptomerion.

EXPERIMENTAL

Optical rotations were taken in dioxane unless otherwise stated. NMR spectra were recorded on a Varian

A-60 spectrometer and a Varian HA-100 spectrometer (double irradiation experiment) in C_6D_6 with TMS as internal reference. Preparative GLC was run using an Aerograph Autoprep A-700 instrument. Aluminium-oxide Woelm neutral and Kieselgel 0·2–0·5 mm (Merck) were used for column chromatography. M.ps were measured with a Kofler hot stage apparatus and are not corrected.

Isolation of delobanone (I) *and acetoxydelobanone* (II). Dried and chipped roots of *Lindera triloba* (7·1 kg) were extracted with ether (12 l × 3). The extract was evaporated to give a brown oil (104·85 g), which was divided into a light petroleum soluble fraction (A, 62·06 g) and an ether soluble fraction (B, 35·85 g). Fraction B was dissolved in ether and washed with 5% $NaCO_3$ aq. The neutral oil (27·18 g) thus obtained was chromatographed on silica gel (820 g) and eluted successively with light petroleum–ether (9:1, 3:1 and 1:1) and ether. The fraction eluted with light petroleum–ether (1:1) (10·19 g) was again chromatographed on silica gel (300 g). Elution with light petroleum–ether (9:1 and 3:1) yielded a pale brown oil (7·39 g), which was separated by prep TLC [Kieselgel GF_{254}–UV, $CHCl_3$–EtOH (98:2)]. The compound of R_f 0·41 was delobanone (I), a colourless oil (2·67 g), $[\alpha]_D^{24}$ + 10·2° ± 0·5° (*c*, 0·998) (Found: C, 76·28; H, 10·16. $C_{15}H_{24}O_2$ requires: C, 76·22; H, 10·24%). The spectral data are shown in the text. The compound of R_f 0·56 was acetoxy-delobanone (II), a colorless oil (2·61 g), $[\alpha]_D^{23}$ + 207° ± 1·7° (*c*, 1·442). The spectral data are shown in the text. The 2,4-dinitrophenylhydrazone of II had m.p. 160–161°. (Found: C, 58·33; H, 6·32; N, 11·78. $C_{23}H_{30}O_7N_4$ requires: C, 58·21; H, 6·37; N, 11·81%).

Fraction A was washed with 5% Na_2CO_3 aq. to give a neutral oil (54·7 g). The oil (38·54 g) was chromatographed on silica gel (1200 g) and eluted with light petroleum, light petroleum–ether (9:1, 3:1 and 1:1) and ether. The head eluate from light petroleum–ether (1:1) (6·32 g) was heated with Girard T reagent (12 g) in a mixture of 95% EtOH (30 ml) under reflux for 3 hr. The mixture was made alkaline with 15% Na_2CO_3 aq. and extracted with ether to remove the ether soluble component (1·58 g). The water layer was acidified with conc HCl, allowed to stand at room temp for 1 hr, and extracted with ether. The ether layer was washed with 5% $NaHCO_3$ aq., dried (Na_2SO_4) and evaporated leaving an orange oil (4·80 g). The oil was dissolved in 5% KOH–MeOH (30 ml) and allowed to stand at room temp under N_2 atm for 1 hr. Water (30 ml) was added to the mixture, which was then extracted with ether. The ether layer was washed, dried (Na_2SO_4) and evaporated to give an oil (4·20 g), which was chromatographed on alumina (120 g) and eluted with light petroleum, light petroleum–ether (9:1, 3:1 and 1:1) and ether. The eluate from light petroleum–ether (3:1) gave delobanone (I) as an oil (2·19 g) (IR spectrum). The eluate from light petroleum–ether (1:1) (1·04 g) was purified by prep TLC [Kieselgel GF_{254}–UV and $CHCl_3$–EtOH (95:5)]. The compound of R_f 0·41 was 1α-hydroxydelobanone (V), colourless needles, m.p. 97–98° (from ether-n-hexane), $[\alpha]_D^{23}$ + 33·9° ± 1·2° (*c*, 0·602), λ_{max} (95% EtOH) 225 mμ (ε 7510), ν_{max} ($CHCl_3$) 3600, 3420 (OH) and 1676 cm^{-1} (αβ-unsaturated ketone), τ 8·77 (3H, s, 15-Me), 8·45 (3H, d, J = 2 Hz) and 8·34 (3H, d, J = 2 Hz) (12-Me and 13-Me), 8·23 (3H, d, J = 1·8 Hz, 14-Me), 7·47 (1H, d-d, J = 17 and 4 Hz, 5-H_{eq}), 7·11 (1H, d-d, J = 17 and 13 Hz, 5-H_{ax}), 5·71 (1H, d-d, J = 6 and 3 Hz, 1-H), 4·89 (1H, m, 10-H) and 3·68 (1H, d-q, J = 6 and 1·8 Hz, 2-H). (Found: C, 71·26; H, 9·57. $C_{15}H_{24}O_3$ requires: C, 71·39; H, 9·59%).

Catalytic hydrogenation of delobanone (I). Delobanone (I, 203 mg) was hydrogenated over 1·5% Pd-C (200 mg) in EtOH (10 ml) at room temp. The reaction stopped after 2·4 moles (48·9 ml) of H_2 had been absorbed. The mixture was filtered to remove the catalyst. The filtrate was evaporated to give an oily product (213 mg) which was dissolved in 5% KOH–MeOH (6 ml) and heated under reflux for 2 hr. Water was added to the mixture, which was then extracted with ether. The extract was washed, dried (Na_2SO_4) and evaporated to give an oil (193 mg), purified by chromatography on alumina yielding tetrahydrodelobanone (III) as a colourless oil. $[\alpha]_D^{28\cdot3}$ − 15·1° ± 2·4° (*c*, 0·225), ν_{max} (film) 3500 (OH) and 1714 cm^{-1} (cyclohexanone); τ 9·13 (6H, d, J = 6 Hz, 12-Me and 13-Me), 9·05 (3H, d, J = 5 Hz, 14-Me) and 8·90 (3H, s, 15-Me); ORD. $[\phi]_{400}$ − 267°, $[\phi]_{313}$ − 2453°, $[\phi]_{274}$ + 2826°, and $[\phi]_{250}$ + 2240°. 2,4-Dinitrophenylhydrazone had m.p. 83–84° (Found: C, 60·37; H, 7·27; N, 13·27. $C_{21}H_{32}O_5N_4$ requires: C, 59·98; H, 7·67; N, 13·33%).

Dehydration of delobanone (I). $SOCl_2$ (0·2 ml) was added dropwise to an ice-cooled soln of delobanone (I, 297 mg) in dry pyridine (0·5 ml) and the mixture was set aside at 0° for 0·5 hr. Ice was added to the mixture which was then extracted with ether. The extract was washed, dried (Na_2SO_4) and evaporated to give an oil (237 mg), which was chromatographed on alumina (activity IV, 8 g) and eluted with light petroleum and light petroleum-ether (3:1 and 1:1). The light petroleum fraction (99 mg) showed two peaks of retention times 24·6 min (65%) and 30·0 min (35%) in GLC (5% DEGS, 160°, He 100 ml/min). The compound of retention time of 24·6 min was (+)-cryptomerion (IV), an oil, $[\alpha]_D^{23}$ +21·4° ± 0·6° (*c*, 0·986, $CHCl_3$), λ_{max} (dioxane) 235 mμ (ε 8680): ν_{max} (film) 3075, 1645, 900 (>C=CH_2) and 1680 cm^{-1} (αβ-unsaturated ketone): τ 8·48 (3H, d, J = 1·5 Hz) and 8·33 (3H, d, J = 1·5 Hz) (12-Me and 13-Me), 8·20 (3H, d, J = 1·5 Hz, 14-Me), 5·33 (1H, s) and 5·25 (1H, d, J = 1·5 Hz) (15-CH_2), 4·88 (1H, m, 10-H) and 3·66 (1H, m, 2-H), 2,4-Dinitro-

phenylhedrazone had m.p. 168–170°. (Found: C. 61·02; H. 6·61; N. 13·43. $C_{21}H_{26}O_4N_4 \cdot H_2O$ requires: C. 60·56; H. 6·78; N. 13·45%).

The eluate from light petroleum–ether (3:1 and 1:1) (106 mg) was recovered delobanone (I) (IR spectrum).

Saponification of acetoxydelobanone (II). A soln of acetoxydelobanone (II. 70 mg) in 5% KOH–MeOH (1·0 ml) was left at room temp for 45 min. The mixture was worked up in the usual way to give crude product (55 mg), which was purified by prep TLC [Kieselgel GF_{254}–UV and $CHCl_3$–EtOH (95:5)]. The compound of R_f 0·55 gave 1α-hydroxy-delobanone (V) (35 mg) as colourless needles. m.p. 97–98° (from ether-n-hexane) (m.m.p. and IR spectrum).

Catalytic hydrogenation of 1α-hydroxydelobanone (V). 1α-Hydroxydelobanone (V. 301 mg) was hydrogenated over 1·5% Pd–C (297 mg) in EtOH (10 ml). The reaction ceased after 2·2 moles of H_2 had been absorbed. Removal of catalyst and solvent gave a crystalline substance (314 mg). Recrystallization from ether–light petroleum gave a tetrahydro compound (VI) as colourless needles. m.p. 92–93°. $[\alpha]_D^{23}$ + 3·3° ± 0·8° (*c.* 0·520): ν_{max}(KBr) 3400. 3300 (OH) and 1705 cm^{-1} (cyclohexanone): τ 9·13 (6H. d. J = 5 Hz. 12-Me and 13-Me). 8·95 (3H. d. J = 6 Hz. 14-Me). 8·83 (3H. s. 15-Me). 7·63 (1H. d-d. J = 13 and 4 Hz. 5-H_{eq}) and 7·18 (1H. d-d. J = 8 and 13 Hz. 5-H_{ax}): ORD. $[\phi]_{400}$ − 49°. $[\phi]_{313}$ − 1169°. $[\phi]_{275}$ + 2043°. $[\phi]_{245}$ + 1859°. (Found: C. 69·98; H. 11·23. $C_{15}H_{28}O_3$ requires: C. 70·27; H. 11·01%).

Oxidation of 1α-hydroxydelobanone (V) *with* CrO_3. A soln of 1α-hydroxydelobanone (V. 205 mg) in dry pyridine (2 ml) was added dropwise to a CrO_3-pyridine complex prepared from CrO_3 (784 mg) and dry pyridine (8 ml) under ice-cooling and stirring, and the mixture left at room temp for 4 hr. Water was added and mixture extracted with ether. The ether soln was washed, dried (Na_2SO_4) and evaporated to give an oil (140 mg), purified by chromatography on alumina to yield a *p*-quinone derivative (VII) as a yellow oil, ν_{max} ($CHCl_3$) 3500 (OH). 1657. 1611 cm^{-1} (*p*-quinone). τ 8·80 (3H. s. 15-Me). 8·52 (3H. broad s) and 8·43 (3H. broad s) (12-Me and 13-Me). 8·40 (3H. d. J = 1·8 Hz. 14-Me). 4·93 (1H. m. 10-H). 3·95 (1H. q. J = 1·8 Hz, 2-H) and 3·20 (1H, s, 5-H). (Found: C, 72·23; H, 8·07. $C_{15}H_{20}O_3$ requires: C, 72·55; H, 8·12%).

Conversion of acetoxydelobanone (II) *into tetrahydrodelobanone* (III). A soln of acetoxydelanone (II. 259 mg) in toluene (4 ml) was added dropwise over 10 min to a soln of calcium (1·5 g) in NH_3 (100 ml) at − 70° under stirring. NH_4Cl (5 g) was added to the mixture and NH_3 was evaporated. Water was added to the residue and the aqueous layer extracted with ether. The ether extract was washed, dried (Na_2SO_4) and evaporated to give a yellow oil (185 mg). The oil (71 mg) was hydrogenated over 10% Pd-C (100 mg) in EtOH (4 ml) at room temp. The reaction stopped after 9·2 ml of H_2 had been absorbed. Removal of catalyst and solvent yielded a saturated hydroxy-ketone (71 mg), a colourless oil. $[\alpha]_D^{26.7}$ − 17·7° ± 0·5° (*c.* 1·14), identical with tetrahydrodelobanone (III) (IR and NMR spectra). Its 2,4-dinitrophenylhydrazone had m.p. 84°.

Treatment of 1α-hydroxydelobanone (V) *with benzaldehyde.* A mixture of 1α-hydroxydelobanone (V. 184 mg) and newly fused $ZnCl_2$ (188 mg) in benzaldehyde (2·0 ml) was heated at 80° for 0·5 hr under N_2 atm. The mixture was dissolved in ether, washed, dried (Na_2SO_4) and evaporated leaving a pale yellow oil (367 mg). The oil was chromatographed on alumina (activity IV, 12 g) and eluted with n-hexane to give a crystalline substance (112 mg). Recrystallization from ether-n-hexane gave a pure sample of O-benzylidene compound (VIII) as colourless prisms. m.p. 98–99°. λ_{max}(dioxane) 220 mμ (ε 12.300): ν_{max}(nujol) 1677 (αβ-unsaturated ketone). 1092. 1009 (ether). 760 and 695 cm^{-1} (substituted benzene): τ 8·90 (3H. s. 15-Me). 8·45 (3H, broad s) and 8·34 (3H, broad s) (12-Me and 13-Me). 8·22 (3H, d, J = 1·8 Hz, 14-Me). 7·50 (1H, d-d-d, J = 16, 4 and 1 Hz. 5-H_{eq}). 7·09 (1H. d-d. J = 16 and 13 Hz. 5-H_{ax}). 5·88 (1H. d-d. J = 6 and 4 Hz. 1-H). 4·90 (1H. m. 10-H). 4·33 (1H. s. 16-H). 3·64 (1H. d-q. J = 6 and 1·8 Hz. 2-H) and five protons (m) centered at 2·85 and 1·94 due to Ph group. (Found: C. 77·23; H. 8·17. $C_{22}H_{28}O_3$ requires: C. 77·61; H. 8·29%).

NOE experiments. NOE experiments were carried out on a Varian HA-100 spectrometer using about 5% (w/v) carefully degassed soln in C_6D_6 in the frequency-swept and internal C_6H_6 locked mode. The integrated intensities of a signal were measured more than four times with and without irradiation at another signal.

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