[Chem. Pharm. Bull. 31(9)3113—3128(1983)]

Carbon-13 Nuclear Magnetic Resonance Spectra of Pterosin-Sesquiterpenes and Related Indan-1-one Derivatives[1)]

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(Received February 8, 1983)

Methyl derivatives of indan-1-one were prepared as models to aid in interpreting the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of pterosin-sesquiterpenes which were isolated from bracken fern, *Pteridium aquilinum* var. *latiusculum*. The chemical shifts of the carbons of the methylindan-1-ones were assigned by the proton decoupling technique. All the ^{13}C-NMR signals of the pterosin-sesquiterpenes were assigned by means of selective proton decouplings, and from the ^{13}C–^{1}H long-range couplings and ^{13}C chemical shifts of the model compounds.

Keywords——indan-1-one derivative; methylindan-1-one; pterosin-sesquiterpene; methylindan-1-one synthesis; ^{1}H-NMR; ^{13}C-NMR; selective decoupling; C–H decoupling

Pterosin-sesquiterpenes were first isolated from bracken fern, *Pteridium aquilinum* var. *latiusculum* (Pteridaceae),[3)] and so far about 30 pterosin-sesquiterpenes have been isolated from the leaves[4,5)] and the rhizomes,[6)] and more than 20 other pterosin-sesquiterpenes from other ferns.[7)] These sesquiterpenes were established to be 2,5,7-trimethyl-indan-1-one derivatives.[5-7)] Recently, various indan-3-one and indan-1-ol type sesquiterpenes have been isolated from other ferns of the same family.[8)]

The pterosin-sesquiterpenes comprise a structurally new class of naturally occurring sesquiterpenes. Although the proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy played an important role in determining the structures,[5-7)] systematic data on the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of this class of compounds have not yet been reported.

A detailed assignment of the ^{13}C-NMR spectra of various pterosin-sesquiterpenes is presented in this paper. The usefulness of this information for the structural elucidation of new, structurally related terpenoids is discussed.

Results and Discussion

Many of the signals due to the pterosin-sesquiterpenes could be assigned on the basis of the multiplicity of the signals in the ^{1}H off-resonance decoupled (OFR) spectra. However, it was difficult to distinguish among the aromatic carbons, because the benzene ring of the sesquiterpenes is highly substituted. In order to assign the signals of the carbons, the model compounds **1**—**11** shown in Chart 1 were prepared, and the chemical shifts and long rang ^{13}C–^{1}H coupling constants of the aromatic carbons were determined.

The preparation of the model compounds **2**—**11** will be dealt with in the experimental section. Their structures were established by the following evidence. i) The ultraviolet (UV) spectra (Table I) exhibited absorptions at λ 286—298 and 245—258 nm due to the indan-1-one chromophore. ii) The infrared (IR) spectra showed absorptions at ν 1705—1695 and 1610—1580 cm^{-1} due to a carbonyl group and a benzene ring. iii) The ^{1}H-NMR spectra

TABLE I. UV and ^{1}H-NMR Chemical Shifts of Methylindan-1-ones (**1**—**11**)

Compd. No.	λ nm (log ε)	2-H	3-H		4-H	5-H	6-H	7-H	C_2-Me	C_4-Me	C_5-Me	C_6-Me	C_7-Me
1	243 (4.08) 287 (3.31) 294 (3.34)	2.50 (dd) J=6.1 J=5.9	2.97 (dd) J=6.1 J=5.9		7.35 (dd) J=7.2 J=0.8	7.48 (ddd) J=7.7, 7.2 J=1.1	7.25 (td) J=7.5 J=0.8	7.60 (d) J=7.6					
2	245 (4.11) 286 (3.34) 293 (3.41)	2.71 (qdd) J=7.2 J=4.6	2.73 (dd) J=17.8 J=3.9	3.40 (dd) J=17.8 J=8.7	7.45 (d) J=7.6	7.59 (ddd) J=7.3, 7.0 J=1.3	7.36 (dd) J=7.6 J=7.0	7.76 (d) J=7.5	1.31 (d) J=7.3				
3	252 (4.01) 284 (3.39) 293 (3.44)	2.60 (dd) J=6.1	3.03 (dd) J=6.1		7.23 (d) J=0.5		7.13 (d) J=7.8	7.60 (d) J=7.8			2.41		
4	249 (4.12) 289 (3.37) 297 (3.40)	2.64 (dd) J=6.4 J=5.6	3.07 (dd) J=6.4 J=5.6		7.26 (d) J=7.6	7.42 (dd) J=7.6 J=7.3	7.08 (d) J=7.3						2.63
5	254 (4.17) 286 (3.48) 293 (3.44)	2.64 (qdd) J=7.3 J=8.5, 3.9	2.65 (dd) J=17.5 J=3.9	3.31 (dd) J=17.8 J=8.5	7.21		7.14 (d) J=7.8	7.62 (d) J=7.8	1.28 (d) J=7.3	2.41			
6	247 (4.05) 295 (3.45) 303 (3.47)	[a]	2.70 J=17.6 J=3.6	3.32 (dd) J=17.6 J=8.6	7.30 (d) J=7.8	7.38 (d) J=8.1		7.52	1.28 (d) J=7.3			2.37	

7	249 (4.09) 291 (3.33) 298 (3.34)	[a]	[a]	3.31 (dd) J=18.0 J=8.8	7.22 (d) J=7.6	7.40 (t) J=7.6	7.07 (dd) J=7.3 J=0.7		1.28 (d) J=7.3				2.62
8	254 (4.04) 303 (3.40)	[a]	[a]	3.24 (dd) J=17.3 J=7.3		7.24 (d) J=7.6	7.01 (d) J=7.3		1.30 (d) J=6.8	2.29			2.60
9	254 (4.17) 297 (3.31)	2.67 (qdd) J=7.3 J=8.5, 3.7	2.68 (dd) J=17.6 J=3.7	3.31 (dd) J=17.6 J=8.5	7.20			7.50	1.28 J=7.3		2.33	2.29	
10	258 (4.14) 287 (3.29) 298 (3.31)	[a]	[a]	3.21 J=18.0 J=9.0	6.98		6.8		1.25 (d) J=7.1		2.33		2.60
11	252 (4.41) 303 (3.86)	[a]	[a]	3.29 (dd) J=17.3 J=8.8	7.14 (d) J=7.6	7.31 (d) J=7.6			1.28 (d) J=7.3			2.29	2.59

a) The ^{1}H signals of the methine and methylene protons at 2.6—2.7 ppm overlapped each other.
Coupling constants are given in J=Hz. Abbreviations are d=doublet, t=triplet, q=quartet and no description=singlet.

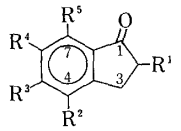
TABLE II. ^{13}C-NMR Chemical Shifts and ^{13}C–^{1}H Coupling Constanm of Methylindan-1-ones (**1**—**12**)

Compd. No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C_2-Me	C_4-Me	C_5-Me	C_6-Me	C_7-Me
1	206.1	36.0 Tdd $1J=130.9$ $2J=4.0$ $2J=3.0$	25.7 Tdd $1J=130.9$ $2J=4.0$ $2J=3.0$	126.6 Dd $1J=161.8$ $3J=7.4$	134.3 Dd $1J=160.5$ $3J=7.4$	127.0 Dd $1J=163.3$ $3J=7.4$	123.2 Dd $1J=163.3$ $3J=7.4$	136.9 m	155.0 n					
2	209.2 q $3J=4.4$	42.0 Ddqd $1J=129.0$ $J=7.2$ $J=4.2$	35.0 Tdq $1J=131.9$ $2J=1.8$ $3J=5.2$	126.5 Dd $1J=161.2$ $3J=8.8$	134.6 Dd $1J=159.7$ $3J=7.3$	127.4 Dd $1J=159.7$ $3J=7.3$	124.0 Dd $1J=158.3$ $3J=7.3$	136.4 m	153.4 m	16.3 Qtd $1J=128.5$ $J=5.3$ $J=2.0$				
3	206.3	36.3 Tdd $1J=130.7$ $2J=4.0$ $2J=3.0$	25.6 Td $1J=131.8$ $2J=2.9$	127.0 Dqm $1J=158.2$ $3J=5.0$	145.6 dq $3J=6.4$ $2J=6.3$	128.5 Dqd $1J=158.8$ $2J=1.3$	123.4 Dd $1J=161.3$ $2J=1.3$	134.8 dm $3J=6.9$	155.6 m			22.0 qt $1J=126.9$ $3J=4.4$		
4	207.7	36.8 Tdd $1J=129.9$ $2J=4.0$ $2J=3.0$	25.4 Tm $1J=132.4$	124.0 Dd $1J=161.7$ $3J=8.1$	133.9 D $1J=159.9$	129.1 Ddq $1J=159.9$ $3J=6.0$ $3J=4.2$	138.9 dqd $3J=6.5$ $2J=6.5$ $2J=1.1$	134.5 m	155.9 m					18.2 qd $1J=128.0$ $3J=5.1$
5	208.7	42.1 Ddqd $1J=131.1$ $2J=7.2$ $2J=4.2$ $2J=2.1$	34.8 Tm $1J=128.9$	126.9 Dqm $1J=158.2$ $3J=5.0$	145.7 dq $2J=6.1$ $2J=6.0$	128.6 Dqm $1J=158.9$ $3J=5.0$	123.8 Dd $1J=161.5$ $2J=1.3$	134.1 m	153.9 ddd $3J=8.7$ $J=5.5$ $J=3.7$	16.4 Qtd $1J=128.0$ $J=5.3$ $J=1.8$		22.0 Qt $1J=126.9$ $3J=4.2$		
6	209.0	42.2 Ddq $1J=126.0$ $2J=7.2$ $2J=4.2$	34.6 Tm $1J=131.9$	126.2 Dm $1J=159.7$	135.8 Ddq $1J=155.3$ $3J=7.4$ $3J=4.4$	137.2 m	123.8 Dm $1J=161.2$	135.8 m	150.7 m	16.3 Qtd $1J=128.0$ $J=5.3$ $J=1.8$			21.0 Qt $1J=126.0$ $3J=4.4$	

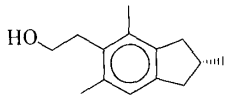
7	210.1 q $3J=4.4$	42.3 Ddq $1J=128.7$ $2J=7.2$ $2J=4.2$	34.6 Tm $1J=131.2$	123.8 Dd $1J=161.3$ $3J=7.3$	133.9 D $1J=159.9$	129.2 Ddqd $1J=159.9$ $3J=6.5$ $3J=5.5$ $2J=1.1$	139.0 dq $3J=6.6$ $2J=6.6$	133.8 m	154.1 m	16.4 Qtd $1J=128.0$ $J=5.3$ $J=1.8$				18.2 Qd $1J=127.8$ $J=5.1$
8	210.5	42.1 Ddq $1J=129.0$ $J=4.4$ $J=2.9$	33.5 Td $1J=130.4$ $J=3.9$	132.6 m	134.4 D $1J=155.3$	129.3 Dq $1J=158.3$ $3J=5.9$	136.1 m	133.5 m	152.9 m	16.5 Qtd $1J=128.0$ $J=5.9$ $J=1.7$	17.4 Qd $1J=126.0$ $3J=4.4$			17.8 Qd $1J=127.8$ $3J=5.1$
9	208.8	42.2 Ddq $1J=128.6$ $2J=7.1$ $2J=4.2$	34.6 Tqd $1J=130.7$ $3J=5.0$ $2J=2.5$	127.3 Dqd $1J=153.8$ $3J=4.7$ $J=0.9$	144.7 m	136.2 m	124.3 Dq $1J=159.1$ $3J=5.5$	134.5 m	151.5 q[a] $J=5.9$	16.4 Qtq $1J=128.0$ $J=5.3$ $J=1.7$		20.6 Qdd $1J=126.7$ $3J=5.2$ $2J=0.9$	19.6 Qd $1J=126.5$ $3J=5.0$	
10	209.2	42.4 Ddq $1J=128.5$ $J=3.0$ $J=1.1$	34.4 Tq $1J=131.2$ $3J=5.0$ $2J=1.0$	124.1 Ddq $1J=158.4$ $3J=10.3$ $3J=4.7$	144.8 qdd $2J=5.9$ $2J=0.9$ $2J=0.6$	130.3 Ddm $1J=156.2$ $3J=10.3$	138.5 qd $2J=6.3$ $3J=0.6$	131.5 m	154.4 ddd $J=6.1$ $J=4.8$ $J=0.6$	16.4 Qtd $1J=128.0$ $J=5.3$ $J=2.0$		21.7 Qt $1J=126.7$ $3J=4.5$		18.0 Qd $1J=127.8$ $3J=5.1$
11	210.5 q $3J=4.4$	42.7 D $1J=128.5$	34.0 T $1J=130.7$	123.3 Ds $1J=160.6$	135.7 Dq $1J=157.1$ $3J=5.0$	136.1 m	137.3 m	133.6 qd $3J=4.2$ $J=1.7$	151.8 m	16.4 Qtd $1J=128.0$ $J=5.3$ $J=2.0$			18.9 Qd $1J=126.7$ $3J=5.0$	13.5 Qs $1J=127.5$
12	210.2 q $3J=4.4$	42.6 Ddqd $1J=128.4$ $J=7.1$ $2J=4.2$ $J=1.3$	33.9 Tqd $1J=131.3$ $3J=5.1$ $2J=1.1$	125.7 Dqd $1J=157.1$ $3J=4.6$ $J=1.1$	144.4 q $2J=5.5$	135.0 m	137.9 q $2J=5.3$	132.2 m	152.5 ddd $J=5.5$ $J=4.2$ $J=1.5$	16.5 Qtd $1J=128.0$ $J=5.3$ $J=1.8$		21.3 Qd $1J=127.0$ $3J=5.0$	[b]	13.7 Qs $1J=127.8$

a) The coupling pattern is quartet-like.
b) The chemical shifts of the hydroxyethyl carbons are 31.9 (T, $1J=127.3$ Hz) and 61.6 ppm (Td, $1J=142.9$ and $2J=5.9$ Hz).

Coupling constants are given in J=Hz. Abbreviations are s=singlet, d=doublet, t=triplet q=quartet and m=multiplet (capital letters: one bond C–H coupling=$1J$ and small letters: two and three bonds C–H coupling constants=$2J$ and $3J$, respectively).



Compd. No.	R^1	R^2	R^3	R^4	R^5
1	H	H	H	H	H
2	Me	H	H	H	H
3	H	H	Me	H	H
4	H	H	H	H	Me
5	Me	H	Me	H	H
6	Me	H	H	Me	H
7	Me	H	H	H	Me
8	Me	Me	H	H	Me
9	Me	H	Me	Me	H
10	Me	H	Me	H	Me
11	Me	H	H	Me	Me



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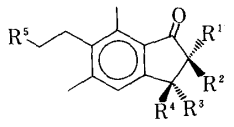

Compd. (No.)	R^1	R^2	R^3	R^4	R^5
Pterosin A (**13**)	CH_2OH	Me	H	H	OH
Pterosin B (**12**)	Me	H	H	H	OH
(2*S*, 3*S*)-Pterosin C (**14a**)	H	Me	OH	H	OH
(2*R*, 3*S*)-Pterosin C (**14b**)	Me	H	OH	H	OH
Pterosin D (**15**)	Me	Me	OH	H	OH
Pterosin F (**16**)	Me	H	H	H	Cl
Pterosin G (**17**)	CH_2OH	H	H	H	OH
Pterosin K (**18**)	CH_2OH	Me	H	H	Cl
Pterosin L (**19**)	CH_2OH	Me	OH	H	OH
Pterosin N (**20**)	Me or OH		H	H	OH
Pterosin Z (**21**)	Me	Me	H	H	OH
Acetylpterosin B (**22**)	Me	H	H	H	OAc
Palmitylpterosin B (**23**)	Me	H	H	H	O-Palmityl
Pteroside A (**24**)	CH_2OH	Me	H	H	O-Glucose
Pteroside B (**25**)	Me	H	H	H	O-Glucose
(2*R*, 3*R*)-Pteroside C (**26a**)	Me	H	H	OH	O-Glucose
(2*S*, 3*R*)-Pteroside C (**26b**)	H	Me	H	OH	O-Glucose

Chart 1

(Table I) exhibited signals at (δ) 2.60—2.62 ppm due to a methyl group or at 7.5 ppm due to a proton at position 7, and signals at 2.4 ppm or 7.0—7.3 ppm due to a methyl group or a proton at position 4, 5 or 6 of the benzene ring, respectively. The vicinal relation between a methyl group and a proton was established by observation of the nuclear Overhauser effect (NOE). iv) The ^{13}C-NMR chemical shifts and their couplings in the model compounds, which were determined on the basis of selective irradiation at various power levels at the proton

frequency and the ^{1}H-gated decoupled spectra with NOE (NOE spectra), were harmoniously assigned as summarized in Table II.

The ^{13}C assignments are discussed below for the carbons in the model compounds **1**—**11** and pterosin B (**12**), a representative of this type of terpenoid, and then the carbon signals of other naturally occurring pterosin-sesquiterpenes **13**—**26** are discussed in comparison with those of **12**.

The proton noise-decoupled spectrum of **12** was obtained in $CDCl_3$ and CD_3OD at 27 °C and its chemical shifts, relative to internal $SiMe_4$, are presented in Tables II and III. Its spectrum was also obtained in mixtures of CD_3OD and $CDCl_3$, in order to correlate the spectra in the two solvents.

Chemical Shift Assignments for Carbons 1, 2 and 3, and Hydroxyethyl Carbons at Carbon 6

i) The lowest-field signal at 210.2 ppm in **12** was assignable to C(1) by comparison with the spectra of indan-1-one (**1**),[9] cyclopenten-1-one,[10] and the model compounds **2**—**11**. The signal of C(1) suffered downfield shifts of +3.1 and +1.6 ppm for methylation at C(2) and at C(7) in **1**, respectively. It is already known[11] in arylalkylketones that *ortho* substitution generally causes large downfield shifts of the carbonyl carbon resonance as a result of steric interaction between the alkylcarbonyl group and the benzene ring. Moreover the carbonyl carbon was found to exhibit ^{13}C–^{1}H couplings with the methyl protons at C(2) in the NOE spectra of 2-methylindan-1-ones **2**, **7**, and **11**, and pterosin B (**12**).

ii) The chemical shift of C(2) in indan-1-ones **1**, **3** and **4** was assigned from a triplet signal in the OFR spectra and by decoupling of the protons at C(2), the ^{1}H signal of which disappeared on deuterium exchange with NaOH–D_2O. The ^{13}C signal of C(2), originally at 36.0 ppm, moved to 42.0 ppm (α-effect: +6.0) on methylation at C(2). In 2-methylindan-1-ones **2**, **5**—**11** and **12** the signal of C(2) appeared at 42.0—42.7 ppm as a doublet in the OFR spectra. However, the NOE spectra of the signal exhibited ^1J C–H and ^2J C–H couplings with the methine proton at C(2), and with the methyl protons at C(2) and the methylene protons at C(3), respectively (Fig. 1a). The couplings were ascertained by decoupling of the methyl protons and the pseudoequatorial proton of the methylene protons. As for the decoupling of the pseudoaxial proton, the ^{1}H signal of the proton overlapped with that of the methine proton at C(2). The decoupling of the proton counteracted the ^1J C–H coupling of C(2) along with that of C(3) (*vide infra*) and disclosed the ^2J C–H coupling between the carbon of C(2) and the methyl protons at C(2).

iii) Chemical shifts for C(3) and for hydroxyethyl carbons at C(6) in **12** were confirmed to be 33.9, and 31.9 and 61.9 ppm, respectively, by means of proton decoupling experiments. The signal of C(3) (Fig. 1b) changed to a doublet corresponding to ^1J C–H coupling when irradiated at one proton frequency of the methylene protons at C(3) (a pseudoequatorial proton at *ca.* 3.4 ppm and a pseudoaxial proton at *ca.* 2.7 ppm). Furthermore, the signal of C(3) was coupled with the methine and methyl protons at C(2). The two carbons of the hydroxyethyl group were observed as a triplet of triplets (61.6 ppm, ^1J=142.9 and ^2J=5.9 Hz) and a triplet (31.9 ppm, ^1J=127.3 Hz). The ^1J C–H couplings of the hydroxyethyl carbons were extinguished by decoupling of the hydroxyethyl protons (3.72 and 2.99 ppm).[5] These coupling constants were also observed in phenethyl alcohol (63.0 ppm, ^1J=142.7 and ^2J=5.2 Hz, and 38.9 ppm, ^1J=127.2 Hz).[12] However there were differences in the chemical shifts and the coupling constants because of the steric effect of *ortho*-substituents.[11,13]

Chemical Shift Assignments for Methyl Carbons

Three signals at 21.3, 16.6 and 13.7 ppm in **12** were allocated to methyl carbons at C(5), C(2) and C(7) by decoupling of the corresponding methyl protons at 2.46, 1.25 and 2.67 ppm, respectively.

i) The methyl carbon at C(2) resonated at 16.3—16.6 ppm in **2**, **5**—**11** and **12**. The signal in the NOE spectra was observed as a quartet of triplets of doublets (^1J=128.0, J=5.3 and J=1.8 Hz) (Fig. 1c—1e). The triplet part of the coupling pattern was proved to be associated with the pseudoequatorial proton at C(3) and the pseudoaxial proton at C(2) or C(3). However, the distinction of the pseudoaxial proton at C(2) from that at C(3) was impossible because the ^{1}H signals of the protons overlapped each other, as already mentioned.

ii) The signal of the methyl carbon at C(4) in **8**, as shown in Table II, was distinguished from that of the carbon at C(7) by irradiation of the signal of the corresponding methyl protons or the proton *meta* to the methyl group. When the ^{1}H methyl signal (at 2.29 ppm) at C(4) or the proton signal (at 7.24 ppm) at C(5) was saturated, the signal due to the methyl carbon at C(4) was collapsed into a doublet due to ^3J C–H coupling or into a quartet due to ^1J C–H coupling, respectively, but no change was observed for the methyl carbon at C(7). On the other hand, the signal of the methyl carbon at C(7) was confirmed by decoupling the proton at C(6) and the methyl protons at C(7) (Table I), and was proved to have larger ^1J C–H and ^3J C–H coupling constants than those of the methyl carbon at C(4) (Table II) (the coupling pattern of the methyl carbon at C(4) was similar to that of the methyl carbon at C(7); see Fig. 1d).

iii) The methyl carbon at C(5) in **3**, **5** and **10** was observed at 21.7—22.0 ppm as a quartet signal coupled with ^1J=126.7—126.9 Hz, and when there is an aromatic proton at C(4) and/or C(6), the methyl carbon also couples with a ^3J C–H coupling constant of 4.2—4.5 Hz (Fig. 1c and 1h). The coupling constant was increased to 5.0—5.2 Hz by an *ortho*-substituent in the cases of **9** and **12**. The chemical shift of the methyl carbon signal in **3**, **5** and **11** was shifted upfield −1.4 ppm due to the substituent of C(6) when compared with those of **9** and **12**.

iv) The methyl carbon at C(6) in **6** appeared as a quartet of triplets signal, coupled (J= 4.4 Hz) with the protons at C(5) and C(7) (Table II). The substituent *ortho* to the methyl carbon produced both an upfield shift effect and a larger ^3J C–H coupling constant (J= 5.0 Hz) associated with the *ortho* proton in **9** and **11**.

v) The methyl carbon at C(7) in **4**, **7**, **8** and **10** was observed at about 18.0 ppm as a quartet of doublets signal, ^1J=127.8—128.0 and ^3J=5.1 Hz (Table II) (Fig. 1g and 1h). The signal collapsed to a quartet with ^1J C–H coupling on irradiation of the proton at C(6). The chemical shift of the methyl carbon showed some upfield shift associated with the *peri*-carbonyl group (this will be discussed later). Furthermore the signal of the methyl carbon at C(7) in **11** and **12** resonated at higher field, about 13.6 ppm, than that in the above model compounds **4**, **7**, **8**, and **10**, indicating a steric compression effect.[11] As for the ^3J C–H coupling constant between the methyl carbon at C(7) and the proton of C(6), it was considered that the constant was increased by a π-bond order effect associated with the carbonyl group,[14] when compared with those of the methyl carbons at C(4), C(5) and C(6).

Chemical Shift Assignments for Aromatic Carbons 4—9

i) The chemical shift of C(4) at 126.6 ppm in **1** was ascertained by decoupling the proton at C(4). The signal of C(4) did not shift by more than 1 ppm on methylation at C(2), C(5) and C(6), but suffered an upfield shift of up to −2.9 ppm on methylation at C(7) and a downfield shift of up to +8.8 ppm on methylation at C(4). The signal of C(4) in the NOE spectrum of **1** was observed as a doublet of doublets, ^1J=161.8 and ^3J=7.4 Hz, coupled with the protons at C(4) and C(6), respectively. In **2**, **4**—**7** and **11**, the ^1J C–H coupling constant of C(4) was 159.7—161.8 Hz, but it was somewhat decreased by methylation at C(5) in the cases of **3**, **5**, **9**, **10** and **12**. The ^3J C–H coupling constants with the proton at C(6) were 7.3—7.4 Hz in **1** and **7**, and 8.1—8.8 Hz in **2** and **4**, and 10.3 Hz in **10**, while the ^3J C–H coupling constants with the methyl protons at C(5) were up to 4.7 Hz in the cases of **3**, **5**, **9**, **10** and **12** (Fig. 1f).

The other aromatic carbon signals C(5), C(6) and C(7) in **1** appeared as doublets of doublets, $^1J=160.5$—163.3, and $^3J=7.3$ Hz between the aromatic carbons and their *meta* protons.

ii) The signal of C(5) appeared at 133.9—135.8 ppm in **1**, **2**, **4**, **6**—**8** and **11**, and suffered a downfield shift of about +11.1 ppm on methylation at C(5). Moreover, the signal suffered a downfield (+1.2—+1.8 ppm) or an upfield (−0.1—−1.0 ppm) shift on methylation at C(6) or at C(7), respectively. The signal of C(5) in 5-methylindan-1-ones **3** and **5** was observed as a doublet of quartets (Fig. 1f) which collapsed to a doublet with ^3J C–H coupling and a quartet with ^2J C–H coupling when decoupled at the methyl protons at C(5) and the proton at C(7), respectively. The signal of C(5) in 7-methylindan-1-ones **4** and **7** was observed as a doublet coupled with $^1J=159.7$—159.9 Hz (Fig. 1g) but the ^1J C–H coupling constant was decreased to 155.3—157.1 Hz by the *ortho* methyl group in the cases of **8** and **11**. This phenomenon was also observed in methylnaphthalenes.[15] The *ortho* methyl protons exhibited the coupling constant of $^3J=5.0$ Hz for the carbon of C(5) in **6** and **8**. The above evidence indicates ^3J C–H coupling (about 7.4 Hz) between the carbon of C(5) and the proton at C(7) in **1**, **2** and **6**, and ^2J C–H coupling (5.5—6.3 Hz) between the carbon of C(5) and the methyl protons at C(5) in **3**, **5**, **10** and **12**.

iii) The chemical shifts and the coupling constants of C(6) were observed as shown in Table II. The chemical shift of C(6) suffered downfield shifts of +1.2 ppm on methylation at C(5), +9.8 at C(6) and +1.8 at C(7) by comparison among the compounds **2**, **5**, **6** and **7**. In **6**, the signal of C(6) was collapsed on irradiation of the proton at C(4) into a quartet coupled with the methyl protons, and was also collapsed into a doublet of ^3J C–H coupling with the proton at C(4) by saturation of the methyl proton at C(6). The signal of C(6) in pterosin B (**12**) will be discussed along with that of C(8).

iv) The signal of C(7) appeared at 123.2—124.3 ppm coupled with $^1J=163.3$—158.3 and $^3J=7.4$ for the proton at C(5) or $^3J=5.5$ Hz for the *ortho* methyl protons in **1**—**3**, **5**, **6** and **9**. The coupling constants of the signal were ascertained by decoupling the proton at C(7), the methyl protons and the proton at C(5), respectively. The carbon signal suffered a downfield shift of +14.8—15.7 ppm with $^2J=6.6$ Hz on methylation at C(7). However, the shift was small, +13.5 ppm, when the signal in **6** was compared with that in **11**, suggesting an effect due to *ortho* steric compression.[11] The signal of C(7) in 7-methylindan-1-ones **4** and **7** was observed as a doublet of quartets (*cf.* Fig. 1g and 1h) which was collapsed to a doublet or quartet when the methyl protons at C(7) or the proton at C(5) were saturated.

v) Two signals at 136.9 and 155.0 ppm in **1** were assigned to C(8) and C(9), respectively, from the chemical shifts.[9] However the signals in the NOE spectrum were observed as multiplets coupled with the protons at C(2), C(3), C(4), C(5), C(6) and C(7). When the proton at C(2) or C(3) was saturated, the multiplet signals of C(8) and C(9) were simplified to two triplet signals coupled with the two protons at C(4) and C(6), and with the two protons at C(5) and C(7), respectively. The signal of C(8) in **5**, a triplet of doublets ($J=7.3$ and 0.7 Hz) (Fig. 1f), was collapsed into a doublet on saturation of the proton at C(4) or C(6), respectively. The signal of C(9) in **5** exhibited coupling constants of $^3J=8.7$ and $^2J=5.5$ and 3.7 Hz with the protons at C(7) and C(3) respectively (Fig. 1f). These coupling constants were ascertained by decoupling the proton at C(7) and C(3), respectively. Other coupling patterns of C(8) and C(9) are shown in Fig. 1g and 1h.

The chemical shifts of C(8) and C(9) were proved to shift upfield or downfield as a result of methylation at various positions: methylation at C(2) induced upfield shifts of −0.5 ppm for C(8) and −1.6 ppm for C(9) of indan-1-one **1**; at C(4), −0.3 ppm for C(8) and −1.2 for C(9); at C(5), −2.1—−2.3 for C(8) and +0.6—+0.5 for C(9); at C(6), −0.6 for C(8) and −2.7 for C(9); at C(7), −2.4—−2.6 for C(8) and +0.7—+0.9 for C(9). This suggested that the different γ-effect of the methyl group at C(2) on the carbons of C(8) and C(9) might be

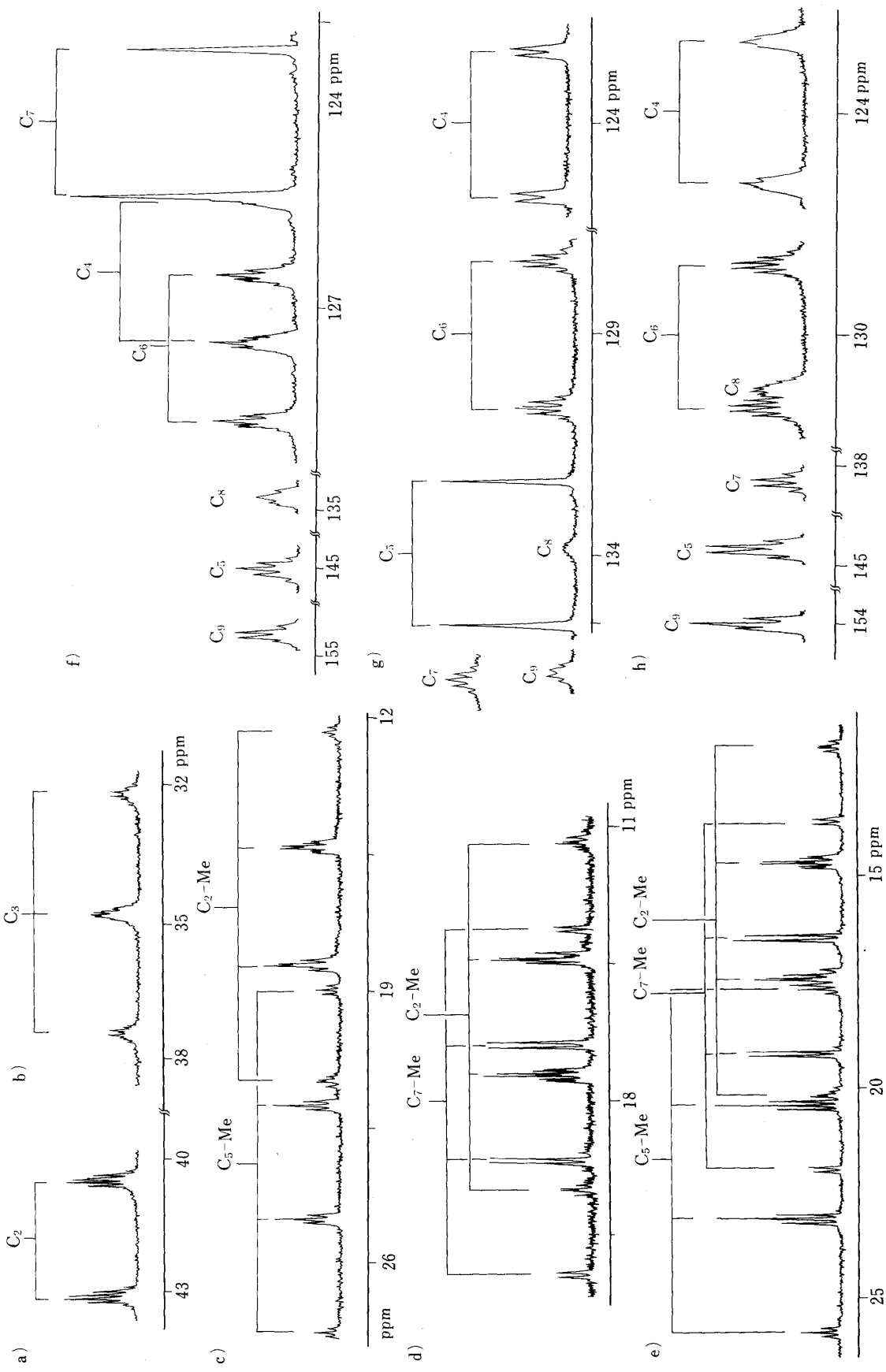

Fig. 1. The Coupling Patterns of 2-Methylindan-1-ones

a) and b) The ^{13}C-NMR-NOE spectra of 2-methylindan-1-ones (2), (5)—(11) and (12). c) and f) The NOE spectra of 2,5-dimethylindan-1-one (5). d) and g) The NOE spectra of 2,7-dimethylindan-1-one (7). e) and h) The NOE spectra of 2,5,7-trimethylindan-1-one (10).

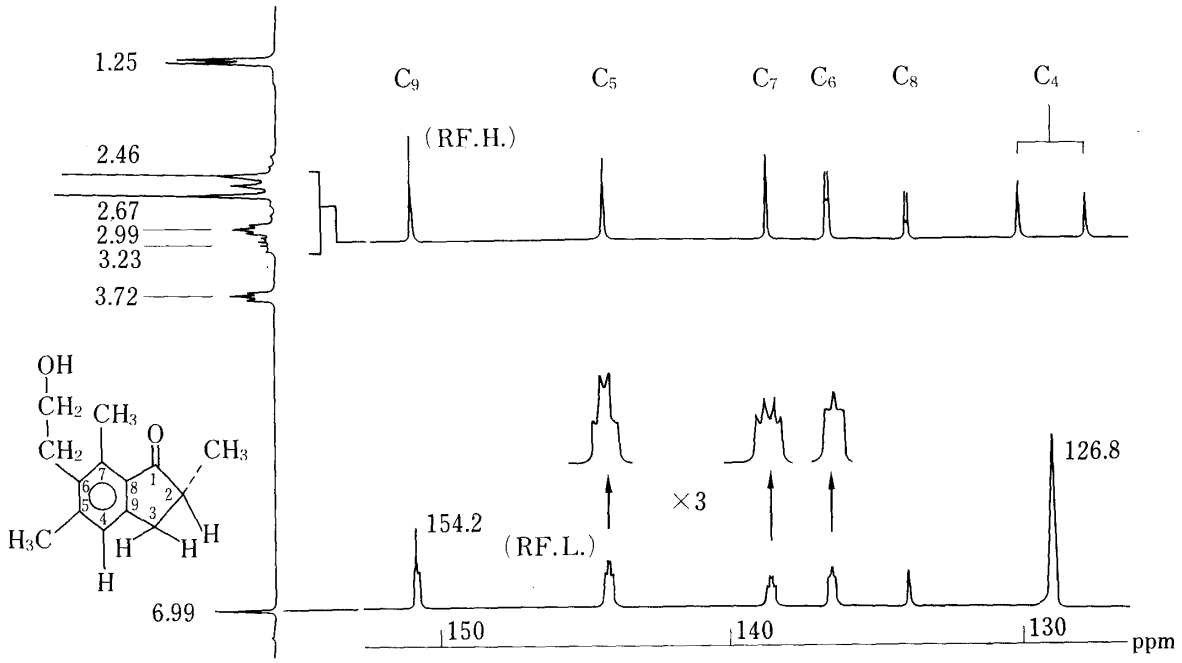

Fig. 2. ^{1}H-NMR and ^{1}H-Selective-decoupled ^{13}C-NMR Spectra of Pterosin B (**12**)

Abbreviations are RF.H.=selective irradiation at high power, and RF.L.=selective irradiation at low power.

associated with a helicity between the carbonyl group and the benzene ring, and indicated that the upfield shifts due to the *ortho* and *para* methyl groups were consistent with the effects due to alkyl groups.[11b]

Although all carbon signals, except for the carbon of C(6), in pterosin B (**12**) appeared to be in accordance with the chemical shifts deduced above, the signal of C(6) appeared at higher field than the corresponding signal in **6**, **9** and **11**, suggesting an effect[16] due to the γ-hydroxy group of the hydroxyethyl group at C(6). Therefore the signal of the carbon of C(6) was ascertained by the selective irradiation method as already mentioned: high-power irradiation of the methyl signal (2.4 ppm) at C(5) corresponded to a partial decoupling at the frequency range from the methyl signal (2.6 ppm) at C(7) to the proton signals (2.3 ppm) at C(3) and C(2), and the signals of C(6) and C(8) changed into two doublets coupled with the proton at C(4) as shown in Fig. 2. In contrast, low-power irradiation of the proton at C(4) caused the signals of C(6) and C(8) to become coupled with the number of substituent protons attached to the carbon (Fig. 2), leaving the others relatively unchanged. These coupling constants were in agreement with values of the ^{2}J C–H couplings due to side chain protons in toluene,[17] and of the ^{3}J C–H couplings between the carbon and *ortho*-methyl protons[18] and between the carbon and *meta*-proton in the benzene ring.[18,19]

Chemical Shift Assignments for the Carbinyl Carbons of the Pterosin-Sesquiterpenes

The ^{13}C-NMR spectra of the pterosin-sesquiterpenes were measured in CD_3OD in order to obtain harmonious data (Table III). However, the solvent effects in the protic solvent were found to be downfield shifts as shown in Fig. 3, relative to pterosin B (**12**) in $CDCl_3$ solution. The ^{13}C assignments relative to the carbons of the indan-1-one skeleton were performed by comparison wth those of **12**. Other carbons were assigned as follows:

i) In pterosin A (**13**), it was somewhat difficult to distinguish the HO–CH_2-carbon of the hydroxymethyl group at C(2) from that of the hydroxyethyl group at C(6) because ^{1}H signals due to these groups appeared with a difference of only 0.08 ppm.[5] The signals of the

TABLE III. ^{13}C-NMR Chemical Shifts of Pterosin-Sesquiterpenes

Compd. No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C_2-R^1	C_2-R^2	C_5-Me	C_6-CH_2-CH_2-R^5	C_7-Me	
12	212.4	43.7	34.7	126.8	146.0	136.3	138.6	132.8	154.2	16.8		21.3	32.9	61.6	13.8	
13	212.7	52.6	37.5	126.8	146.0	136.2	138.6	133.1	153.8	68.2	21.3	21.4	32.9	61.6	13.9	
14a	208.2	55.5	76.9	126.4	146.9	138.8	136.9	131.1	152.8	14.9		21.1	33.9	62.9	14.9	
14b	210.5	50.4	71.2	127.3	146.9	138.8	139.3	131.1	153.4		12.1	21.1	33.9	62.9	15.7	
15	211.6	52.4	77.5	126.1	146.3	138.2	138.3	131.4	153.7	23.5	20.8	21.4	33.1	61.6	14.1	
16[b]	210.0	42.5	33.8	125.9	143.8	134.5	137.7	132.2	153.0	16.5		21.1	32.2	42.0	13.6	
17[c]	209.8	49.9	29.7	126.9	146.1	136.3	138.5	133.9	155.2	63.1		21.4	32.9	61.7	13.9	
18[c]	211.7	50.6	36.9	126.0	144.5	134.8	138.1	131.7	152.7	68.0	21.0	21.2	32.2	42.0	13.7	
19[c]	209.8	56.9	77.6	125.9	146.4	138.0	138.3	132.7	154.7	67.1	19.2	21.5	33.1	61.6	14.2	
20[c]	[d]	77.5	41.1	125.4	145.6	135.4	138.7		149.9	26.1		21.4	31.8	61.5	14.1	
21[c]	212.3	45.6	41.7	125.8	144.4	134.8	138.3	131.0	151.3	25.5	25.5	21.3	31.9	61.5	13.7	
22	210.6	42.6	33.9	125.8	144.2	134.0	138.0	132.2	152.7	16.6		21.1	28.0	62.8	13.6	170.9, 20.9
23	210.0	42.7	34.0	125.9	144.3	134.2	138.1	132.3	157.8	16.7		21.2	28.2	62.7	13.7	173.8, 32.0, 29.8, 29.6, 29.5, 29.4, 29.3, 25.0, 22.7, 14.2
24	210.4	51.3	36.3	126.0	144.4	134.9	136.9	131.8	152.5	66.8	21.0	21.0	29.1	66.9	13.3	102.8, 70.1, 76.8, 70.1, 76.8, 61.4
25	209.6	42.5	33.7	126.1	144.5	135.2	137.2	131.8	152.7	16.7		21.3	29.4	67.3	13.6	103.1, 73.8, 77.0, 70.4, 77.0, 61.7
26a	205.8	53.0	74.2	124.0	144.7	136.2	136.3	130.7	153.0	16.7		19.9	28.6	67.1	12.4	102.4, 73.1, 75.9, 69.6, 76.2, 61.1
26b	208.6	47.9	68.5	125.0	144.7	136.2	136.6	130.5	153.6		11.6	19.9	28.6	67.1	12.5	102.4, 73.1, 75.9, 69.6, 76.2, 61.1
27[b]	40.6	33.9	41.4	124.0	134.9	132.0	132.7	141.0	141.5	21.2		20.4	32.9	62.1	16.2	

a) In ppm downfield from tetramethylsilane in CD_3OD. *b*) In $CDCl_3$. *c*) The sample was only available in very small quantity, so the chemical shifts were recorded using a JEOL FX-100 spectrometer. *d*) Not observed because of the very low concentration.

hydroxyethyl carbons at 61.6 and 31.9 ppm in **12** shifted to 42.0 and 32.2 ppm, respectively, in pterosin F (**16**), in which the hydroxy group of **12** was replaced by a chlorine atom, leaving the other carbon signals relatively unchanged. Therefore signal assignments of the carbons of both groups in **13** were obtained by comparison with those of the chloroethyl derivative, pterosin K (**18**). Although it is known[21] that pterosins A (**13**), G (**17**) and K (**18**) in $CHCl_3$ exist predominantly in the conformer with intermolecular hydrogen-bonding, bearing a pseudoequatorial hydroxymethyl group at C(2), the shift effect[22] produced by the hydrogen-bonding was not observed in relation to the carbonyl carbons in the compounds when the signal in **13** was compared to those of **12** and pterosin Z (**21**) (Table IV).

ii) In regard to the effect of the hydroxy group at C(3) in pterosin C (**14**), the compound was isolated from the natural source as an epimeric mixture of 2*S*,3*S* (**14a**) and 2*R*,3*S* (**14b**) compounds.[5] Therefore all signals, except for carbons over four bonds from the epimeric center of C(2), were observed as a pair of signals. The major compound, 2*S*,3*S*-pterosin C (**14a**), in a solution of CD_3OD exhibited the carbonyl signal at 210.5 and the minor (**14b**), 2*R*,3*S*, at 208.2 ppm. The carbinyl carbon of C(3), the carbon of C(2), and the methyl carbon of C(2) were distinguishable from the corresponding carbons of the epimer (Table III). The signal of the methyl carbon was shifted upfield, −4.7 and −1.9 ppm in **14a** and **14b**, respectively, when compared with that of **12**. It is known[21] that the former exists in the conformer bearing a pseudoaxial methyl at C(2) and a pseudoaxial hydroxy group at C(3), and the latter bears pseudoequatorial methyl and pseudoaxial hydroxy groups. This phenomenon was also observed in pterosins D (**15**) and L (**19**), existing in the conformer[21] bearing a pseudoaxial hydroxy group at C(3). It appears a) that the upfield shift with respect to the carbonyl carbon could be explained by a steric interference associated with the pseudoequatorial, as compared with the pseudoaxial, methyl group, b) that the higher field carbons of the pair signals due to both the carbinyl and methine groups in pterosin C (**14**) were attributable to a steric interaction[22] between the carbinyl proton and the methyl group (higher chemical shifts of the pseudoaxial methyl carbon than the pseudoequatorial methyl carbon), and c) that the effect of the hydroxy group was influenced by the neighbouring functional groups.

The effects due to the hydroxy group are summarized in Table IV.

iii) The distinction of the carbons between the methylene group of C(3) and the oxyethyl group at C(6) was made by selective proton decouplings for acylpterosin B **22** and **23**, but it was made by adding the shift effects[20] due to glycosidation for pterosides A (**24**), B (**25**), and C (**26**) because the ^1H chemical shifts of both groups and of the glucose residue overlapped completely.

Chemical Shift Effects Due to the Carbonyl Group

By comparison of the ^{13}C chemical shifts of pterosin B (**12**) with those of the deoxo derivative (**27**) it was shown that the steric interaction of the carbonyl group is probably responsible for the upfield shift (−4.7 and −2.2 ppm) of the methyl carbon resonances at C(2) and C(7), respectively, and the electric interaction affected the upfield shifts of C(3) and C(8).

In general, assignments of the carbons of the pterosin-sesquiterpenes were made by using a combination of selective irradiation at various power levels at the proton frequency, ^{13}C–^1H coupling constants and ^{13}C chemical shifts of the model compounds. The ^{13}C-NMR spectral

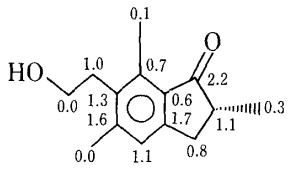

Fig. 3. ^{13}C Chemical Shift Differences for Pterosin B (**12**)

The values (ppm, δCD_3OD–$\delta CDCl_3$) denote downfield shifts for the corresponding carbon signals.

TABLE IV. The Shift Effect[a] Due to Hydroxylation

Carbon	Hydroxylation compounds				
	at C_2-Me 13—21[b]	at C_2-Me 17—12[c]	at C(3) 19—15[c]	at C(3) 15—21[c]	at C(3) 19—13[c]
C_1	+0.4 (γ)	−2.6 (γ)	−1.8 (γ)	−0.7	−2.9
C_2	+7.0 (β)	+6.2 (β)	+4.5 (β)	+6.8	+4.3
C_3	−4.2 (γ)	−5.0 (γ)	+0.1 (γ)	+35.8	+40.1
α-C	+42.7 (α)	+46.3 (α)	+43.6 (α)		
C_2-Me	−4.2		−1.6	−4.7[pa]	−2.1[pa]
				−2.0[pe]	
C_2-CH_2OH					−1.1[pe]
C_9			+2.4	+0.9	

a) The difference is obtained from ^{13}C chemical shifts (ppm) in the same solvent. Abbreviations are α= α-effect of the hydroxy group; β= β-effect; γ= γ-effect; pa=pseudoaxial and pe=pseudoequatorial substituent. *b*) In $CDCl_3$. *c*) In CD_3OD.

results for the present examples of methylindan-1-ones are in good agreement with the assignments based on the selective proton decoupling method for the quaternary carbons in the pterosin-sesquiterpenes.

The present results indicate that ^{13}C-NMR spectroscopy provides an effective method for characterizing the indan-1-ones.

Experimental

Melting points were measured in a Yanaco micro apparatus and are uncorrected. UV spectra were determined in methanol solution and IR spectra in liquid form unless otherwise specified. ^{13}C-NMR and ^1H-NMR spectra were recorded using a JEOL JNM-FX 200 Fourier transform NMR spectrometer at 50 and 200 MHz at 27 °C, respectively. Samples were prepared as approximately 0.5 M solutions in ^2H-chloroform, unless otherwise specified. The field-frequency lock was provided by the ^2H-chloroform. ^{13}C-Chemical shifts were measured relative to Me_4Si at a sweep width of 12000 Hz and FIDs were accumulated into 16 K addresses giving a digital resolution of 1.46 Hz, equivalent to 0.029 ppm. NOE spectra were recorded at a sweep width of 3000 Hz and FIDs were accumulated into 32 K addresses giving a digital resolution of 0.18 Hz. ^1H-Chemical shifts are given in δ values ppm, from Me_4Si at a sweep width of 2000 Hz using 16 K addresses, giving a digital resolution of 0.24 Hz, equivalent to 0.001 ppm. Mass spectra were determined on a JEOL D300 high-resolution mass spectrometer with a direct inlet system for electron impact mass spectroscopy (MS).

Indan-1-one was purchased from Wako Pure Chemical Industries, Ltd.

2-Methylindan-1-one (2)——Indan-1-one (**1**) (4 g) and pyrrolidine (4.5 g) were dissolved in anhydrous benzene (30 ml), and the reaction solution was allowed to stand for 1 h under N_2 gas. The solution was subjected to azeotropic distillation. The product was distilled at 96—98 °C under reducing conditions to afford about 3 g of an oil. The oil was treated with dried benzene (30 ml) and CH_3I (3 g) on a steam bath for 15 min. The reaction mixture was diluted with water and extracted with benzene–ethyl acetate (1 : 1). The organic layer was chromatographed on silica gel (30—70 mesh, 100 g) to afford the starting material (0.6 g) and **2** (0.2 g), bp 127 °C (0.4 mmHg). UV: (Table I). IR ν_{max} cm^{-1}: 2955, 2920, 1700, 1610, 963, 880, 795, 740. *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.93; H, 6.76.

5-, and 7-Methyl-, and 2,5-, 2,6-, and 2,7-Dimethyl-, and 2,5,7-Trimethylindan-1-one (3—7 and 10)——This procedure was carried out according to Nambudiry and Rao.[23] An α-bromo-xylene (0.05 mol) in dimethylformamide (75 ml) was added to a suspension of diethyl methylmalonate (0.05 mol) or diethyl malonate (0.05 ml) and anhydrous potassium carbonate (0.05 mol) in dimethylformamide (75 ml) with stirring at 150—155 °C during a period of 20 min, and the reaction mixture was kept at 150 °C for 10 h with stirring. After removal of most of the solvent by distillation *in vacuo*, water (200 ml) was added to the concentrate, and the product was extracted with ether (3 × 200 ml). Removal of the solvent and fractionation afforded the corresponding diester. The diester (3 g) was refluxed for 24 h with glacial acetic acid (20 ml) and concentrated hydrochloric acid (50 ml). Acetic and hydrochloric acids were distilled off under atmospheric pressure and the organic residue was extracted with ether. Extraction of the ether layer with 5% sodium carbonate followed by acidification liberated a gummy acid, which was re-extracted with ether. Removal of the solvent furnished the acid. From α-bromo-*m*-xylene (10 g): α-methyl-β-(3-methylphenyl)propionic acid (2.1 g); MS

(*m/z*): Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994. Found: 178.0992 and β-3-methylphenylpropionic acid (2.77 g); MS (*m/z*): Calcd for $C_{10}H_{12}O_2$ (M^+): 164.0832. Found: 164.0834. From α-bromo-*p*-xylene (10 g): α-methyl-β-(4-methylphenyl)propionic acid (5.6 g); MS (*m/z*): Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994. Found: 178.0996. From α-bromomesitylene (10 g): β-(3,5-dimethylphenyl)-α-methylpropionic acid (5.0 g); MS (*m/z*): Calcd for $C_{12}H_{16}O_2$ (M^+): 192.1149. Found: 192.1147.

The foregoing acid (2 g) was stirred with polyphosphoric acid at 100 °C for 3 h. The mixture was poured onto crushed ice and water. The resulting indanone was purified by distillation at 0.4 mmHg. The UV and NMR data are listed in Tables I and II.

5-Methylindan-1-one (**3**): 0.91 g, mp 70—71 °C, IR ν_{max} cm^{-1}: 1720, 1690, 1610, 870. *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.10; H, 7.06.

7-Methylindan-1-one (**4**): 0.95 g, mp 51—53 °C, IR ν_{max} cm^{-1}: 1705, 1595, 825. *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.92; H, 6.76.

2,5-Dimethylindan-1-one (**5**): 0.67 g, bp 126 °C, IR ν_{max} cm^{-1}: 2950, 2920, 1705, 1610, 965, 825, 765. *Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.20; H, 7.29.

2,6-Dimethylindan-1-one (**6**): 1.12 g, bp 105 °C, IR ν_{max} cm^{-1}: 2950, 2920, 1705, 1610, 1585, 975, 815, 765. *Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.25; H, 7.43.

2,7-Dimethylindan-1-one (**7**): 0.55 g, bp 109 °C, IR ν_{max} cm^{-1}: 2950, 2920, 1700, 1600, 965, 940, 775. *Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.44; H, 7.52.

2,5,7-Trimethylindan-1-one (**10**): 0.88 g, bp 139 °C, IR ν_{max} cm^{-1}: 2950, 2920, 1700, 1610, 935, 845. *Anal.* Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.44; H, 8.01.

2,4,7-, 2,5,6-, and 2,6,7-Trimethylindan-1-one (8, 9, and 11)——Dry hydrogen chloride gas was bubbled for 4.5 h through a suspension of diethyl (3-methylphenylmethyl)methylmalonate (5 g), paraformaldehyde (1.3 g), and anhydrous zinc chloride (13 g) in tetrachloroethane (70 ml) maintained at 80 °C. The mixture was then cooled and washed with water. After removal of the solvent, the residue was refluxed for 24 h with glacial acetic acid (20 ml) and hydrogen chloride (120 ml). Acetic and hydrochloric acids were distilled off under atmospheric pressure and the organic residue was extracted with ether. Extraction of the ether layer with aqueous sodium carbonate followed by acidification afforded a gummy acid (3.5 g), MS (*m/z*): Calcd for $C_{12}H_{15}ClO_2$ (M^+): 226.0761 (a mixture of β-(4-chloromethyl-3-methylphenyl)-α-methylpropionic and β-(6-chloromethyl-3-methylphenyl)-α-methylpropionic acids). Found: 226.0763. The gummy acid was stirred with zinc (6 g) in acetic acid (40 ml) for 2 d at room temperature. After filtration, removal of the solvent afforded a mixture which was proved to be β-(3,4-dimethylphenyl)-α-methylpropionic acid and its isomer, the 3,6-dimethyl derivative, from the ^{1}H-NMR spectra. The mixture (3 g) was stirred with P_2O_5 (180 g) and H_3PO_4 at 100 °C for 3 h, then poured onto crushed ice and water. The indanones were separated into three compounds by thin layer chromatography followed by distillation.

2,4,7-Trimethylindan-1-one (**8**): 0.10 g, bp 127 °C (0.4 mmHg), IR ν_{max} cm^{-1}: 2950, 2920, 1700, 1595, 960, 817, 775. *Anal.* Calcd for $C_{12}H_{14}O$: C, 82.46; H, 7.55. Found: C, 82.83; H, 8.07.

2,5,6-Trimethylindan-1-one (**9**): 0.58 g, bp 168 °C (0.4 mmHg), IR ν_{max} cm^{-1}: 2950, 2920, 1705, 1610, 940, 885, 765. *Anal.* Calcd for $C_{12}H_{14}O$: C, 82.46: H, 7.55. Found: C, 82.99; H, 7.98.

2,6,7-Trimethylindan-1-one (**11**): 0.70 g, bp 109 °C (0.4 mmHg), IR ν_{max} cm^{-1}: 2950, 2905, 1700, 1605, 1595, 960, 805, 770. *Anal.* Calcd for $C_{12}H_{14}O$: C, 82.46; H, 7.55. Found: C, 82.68; H, 7.98.

Acknowledgement The authors are grateful to Dr. T. Yamaha, Division Chief of Medical Chemistry, and Dr. A. Tanaka, Section Chief of Medical Chemistry, at the National Institute of Hygienic Sciences for their keen interest during the course of this work. The authors also thank Mr. M. Imanari, Manager of the NMR Group at JEOL Company, helpful discussions.

References and Notes

1) This work was presented at the 101st and 102nd Annual Meetings of the Pharmaceutical Society of Japan, April 1981 and April 1982. This paper constitutes Part VII of "Chemical and Toxicological Studies on Bracken Fern, *Pteridium aquilinum* var. *latiusculum*." Part VI: M. Fukuoka, *Chem. Pharm. Bull.*, **30**, 3219 (1982).
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