Five New Compounds from the Heartwood of *Juniperus formosana* HAYATA

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Extracts of the heartwood of *Juniperus formosana* HAYATA were found to contain the known constituents β-sitosterol, α-cedrol, 4-ketocedrol, 3β-hydroxycedrol, isocedrolic acid, δ-cadinol, cadin-8-en-10-ol, clovandiol, sugiol, Δ^5-dehydrosugiol, totarol, 7-oxototarol, cryptojaponol, emodin, and methyl α-conidendral, together with five new compounds, 7α-methoxydeoxocryptojaponol, suginal, detetrahydroconidendrin, formosanol, and junipediol. In addition, 7β-hydroxydeoxocryptojaponol was obtained (first isolation as a natural product). Junipediol has a novel sesquiterpene skeleton which was elucidated by X-ray analysis.

Keywords *Juniperus formosana*; 7α-methoxydeoxocryptojaponol; 7β-hydroxydeoxocryptojaponol; suginal; detetrahydroconidendrin; formosanol; junipediol; X-ray analysis

Juniperus species are interesting in that they always grow at an altitude of 2000—3000 m above sea level. There are ten species of Juniperus indigenous to Taiwan. In connection with our interest in lignans and terpenes, chemical investigations on the heartwood of *Juniperus squamata* LAMB var. *morrisonicola* (HAY.) Li and Keng and *J. formosana* HAYATA were undertaken in our laboratory. From the heartwood of *J. squamata* LAMB var. *morrisonicola* (HAY.) Li and Keng, twelve known compounds in addition to five new sesquiterpenoids (epicedranediol, 3β-hydroxycedrol, 4-ketocedrol, isocedrolic acid, and β-chamigrenic acid) were isolated.[1] In the previous communication we reported the structural elucidation of three new diterpenes [7α-methoxydeoxocryptojaponol (**1a**), 7β-hydroxydeoxocryptojaponol (**1b**),[2] suginal (**2a**)[3]] and two new lignans [detetrahydroconidendrin (**3a**)[4] and formosanol (**4a**)[5]] from the heartwood of *J. formosana*. In this paper we describe the isolation of five new compounds, **1a**, **2a**, **3a**, **4a**, and junipediol (**5a**) (having a novel sesquiterpene skeleton) and **1b** (isolated for the first time from a natural source), together with fifteen known compounds, cryptojaponol (**1c**),[6] methyl α-conidendral (**4b**),[7] β-sitosterol, α-cedrol (**6a**),[1] 4-ketocedrol (**6b**),[1,8] 3β-hydroxycedrol (**6c**),[1,9] isocedrolic acid (**6d**),[1,10] δ-cadinol (**7**),[11] cadin-8-en-10-ol (**8**),[12] clovandiol (**9a**),[13] sugiol (**10a**),[14] Δ^5-dehydrosugiol (**11**),[15] totarol (**12a**),[16] 7-oxototarol (**12b**),[17] and emodin (**13**),[18] from the heartwood of *J. formosana*, and the structural determination of **1a**, **1b**, **2a**, **3a**, **4a**, and **5a**.

7α-Methoxydeoxocryptojaponol (**1a**), mp 160—161 °C, needles from methanol, has the molecular formula $C_{22}H_{34}O_3$ on the basis of elementary analysis. It shows infrared (IR) absorption bands at 3400 (–OH), 3030, 1610, and 1500 cm^{-1} (aromatic absorption) and proton nuclear magnetic resonance (^{1}H-NMR) signals at δ 0.97, 0.97, 1.30 (each 3H, s), 1.25 [6H, d, J=7.0 Hz, –CH(C<u>H</u>$_3$)$_2$], 3.20 [1H, m, –C<u>H</u>(CH$_3$)$_2$], 3.50 and 3.73 (each 3H, s, –OCH$_3$), 4.21 (1H, br s, $W_{1/2}$=5 Hz, H-7), 6.00 (1H, s, –OH, disappeared on D_2O exchange), and 6.70 (1H, s, H-14). The structure of **1a** was suggested to be a derivative of deoxocryptojaponol (**1d**)[19] by the similarity of its ^{1}H-NMR spectral pattern to that of **1d**, except for an extra methoxy group. Treatment of **1a** with acetic anhydride in pyridine at room temperature for 7 d yielded a monoacetate (**1e**) [mp 95—96 °C; ν_{max} 1745 cm^{-1}; no hydroxy absorption signal, δ 2.26 (3H, s)]. Compound **1e** was reduced on catalytic hydrogenation (10% Pd–C in MeOH) to give **1f** (mp 155—157 °C) which exhibited a methylene signal at 2.80 (2H, m), instead of 3.30 (3H, s, –OCH$_3$) and 4.06 (1H, br s, H-7) when compared with that of **1e**. This result suggested that a methoxy group in the benzylic position in **1e** was cleaved by hydrogenolysis. Compound **1f** was identical with deoxocryptojaponol acetate.[19] Such facile hydrogenolysis of a methoxy group is compatible with the presence of a benzylic skeleton in the structure of **1e**. By the action of chromium trioxide in acetic acid, **1f** was converted to the ketone **1g** (mp 167—169 °C) which exhibited a conjugated ketone absorption band at 1690 cm^{-1} in the IR spectrum and an aromatic proton shifted downfield to 7.87 in the ^{1}H-NMR spectrum. Compound **1g** was identical with the acetylation product of cryptojaponol (**1c**).[19] Hydrogenation of **1a** with 10% Pd–C in MeOH gave deoxocryptojaponol (**1d**) (mp 93—95 °C).[19] Compound **1a**, therefore, must have the basic structure of deoxocyptojaponol with an additional methoxy group. The methoxy group is located at C-7, and its orientation was elucidated by the following evidence. The equatorial orientation of the C-7 proton in **1a** is derived from the small coupling with C-6 methylene protons in **1a** ($W_{1/2}$=5 Hz) and **1e** ($W_{1/2}$=4.5 Hz).[20] Consequently, the methoxy group must have the axial orientation. An attempt to prepare the methyl ether of **1a** by treatment with silver oxide and excess methyl iodide in dimethylformamide (DMF) was not successful but gave the unexpected elimination product, 6,7-dehydrodeoxocryptojaponol (**14**) [mp 102—104 °C; δ 5.90 (1H, dd, J=10.0, 4.1 Hz, H-6) and 6.30 (1H, dd, J=10.0, 3.2 Hz, H-7)]. As elimination preferentially occurs in the case of diaxial orientation, the axial orientation of the C-7 methoxy group is suggested. Compound **14** gave **1d** on catalytic hydrogenation. The evidence described above is consistent with the structure assigned for **1a**.

In order to correlate cryptojaponol with royleanone, **1a** was oxidized with *m*-chloroperbenzoic acid, and a red product, 6,7-dehydroroyleanone (**15a**),[21] was isolated.

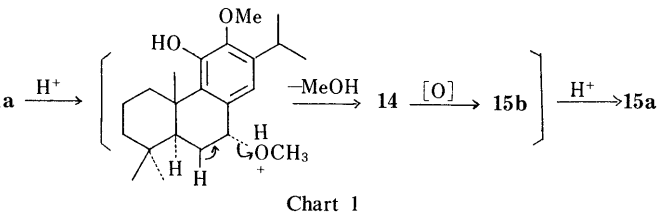
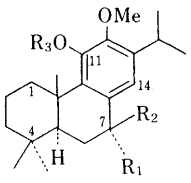
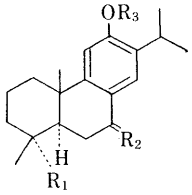


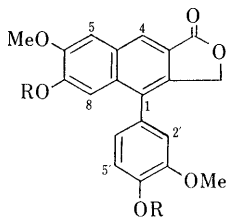
Chart 1



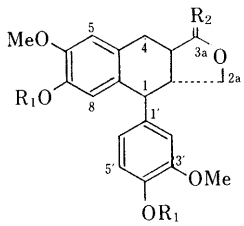
1a : R_1=OMe, R_2=R_3=H
1b : R_1=R_3=H, R_2=OH
1c : R_1+R_2=O, R_3=H
1d : R_1=R_2=R_3=H
1e : R_1=OMe, R_2=H, R_3=Ac
1f : R_1=R_2=H, R_3=Ac
1g : R_1+R_2=O, R_3=Ac
1h : R_1=R_3=H, R_2=OAc
1i : R_1=H, R_2=OAc, R_3=Ac
1j : R_1=H, R_2=OH, R_3=Ac



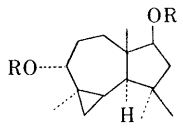
2a : R_1=CHO, R_2=O, R_3=H
2b : R_1=CHO, R_2=O, R_3=Ac
2c : R_1=CH_2OH, R_2=β-OH, α-H, R_3=H
2d : R_1=$-CH<\begin{matrix}S\\S\end{matrix}]$, R_2=O, R_3=H



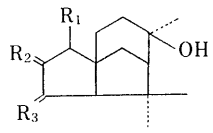
3a : R=H
3b : R=Ac
3c : R=Me



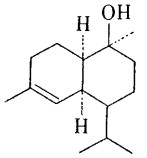
4a : R_1=H, R_2=β-OMe, α-H
4b : R_1=H, R_2=β-H, α-OMe
4c : R_1=Ac, R_2=O
4d : R_1=H, R_2=O
4e : R_1=Ac, R_2=β-OMe, α-H
4f : R_1=Me, R_2=β-OMe, α-H
4g : R_1=Ac, R_2=β-H, α-OMe



5a : R=H
5b : R=Ac



6a : R_1=Me, R_2=R_3=H, H
6b : R_1=Me, R_2=H, H, R_3=O
6c : R_1=Me, R_2=β-OH, α-H, R_3=H, H
6d : R_1=COOH, R_2=R_3=H, H



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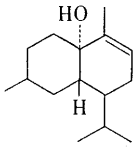

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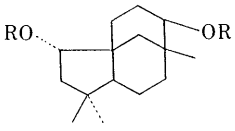
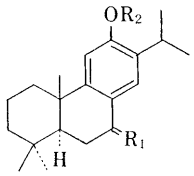
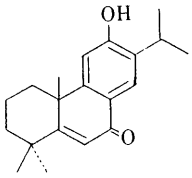


9a : R=H
9b : R=Ac



10a : R_1=O, R_2=H
10b : R_1=$\begin{matrix}S\\S\end{matrix}]$, R_2=H
10c : R_1=H, H, R_2=H
10d : R_1=O, R_2=Ac
10e : R_1=H, H, R_2=Ac



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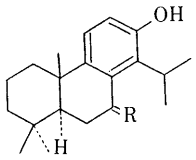
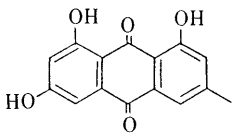


12a : R=H, H
12b : R=O



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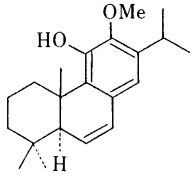

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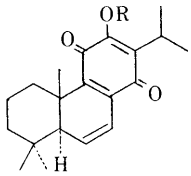
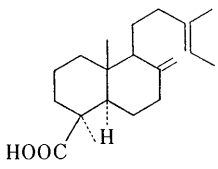


15a : R=H
15b : R=Me



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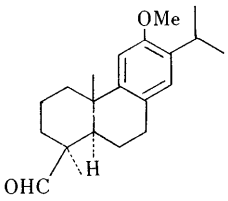

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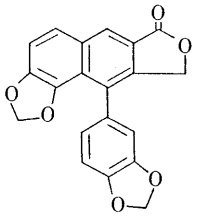

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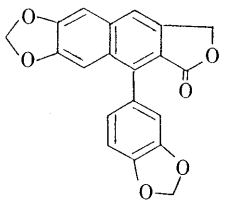

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The proposed pathway of the transformation is depicted in Chart 1. The first intermediate was proposed to be **14** formed *via* elimination of methanol by acid because of the labile nature of the benzylic methoxy group. The prior elimination of methanol was confirmed by the treatment of **1a** with *m*-chlorobenzoic acid in methylene chloride under similar conditions to give **14**. When **14** was treated with *m*-chlorobenzoic acid for longer time, no further reaction occurred. Therefore the hydrolysis must take place from the quinone (**15b**) to give **15a**.

7β-Hydroxydeoxocryptojaponol (**1b**), mp 168—170 °C, $C_{21}H_{32}O_3$, exhibited IR absorption bands at 3540 (–OH), 3240 (–OH), and 3050, 1600 and 1500 cm^{-1} (aromatic) and ^{1}H-NMR spectrum signals at δ 0.93, 0.93, and 1.35 (each 3H, s), 1.15 [6H, d, J=6.0 Hz, –CH(C<u>H</u>$_3$)$_2$], 1.55 and 5.72 (each 1H, s, –OH, disappeared on D_2O exchange), 2.96 [1H, m, –C<u>H</u>(CH$_3$)$_2$], 3.58 (3H, s, –OCH$_3$), 4.41 (1H, m, $W_{1/2}$=16 Hz, H-7), and 6.63 (1H, s, H-14). The structure of **1b** was suggested to be a derivative of deoxocryptojaponol from the similarity of its ^{1}H-NMR spectral pattern to that of deoxocryptojaponol, except for an extra hydroxy group. Treatment of **1b** with acetic anhydride in pyridine at room temperature overnight afforded the monoacetate (**1h**) [mp 116—118 °C; ν_{max} 3400 and 1720 cm^{-1}; δ 2.13 (3H, s)]. The signal of H-7 was shifted downfield to δ 5.90 (dd, J=6.0 and 13.0 Hz). The acetylation of **1h** at a higher temperature (75 °C) with Ac_2O and pyridine yielded the diacetate (**1i**) [mp 122—124 °C; ν_{max} 1760 and 1735 cm^{-1}; δ 2.06 and 2.24 (each 3H, s)]. The diacetate (**1i**) was partially hydrolyzed into another monoacetate (**1j**) [mp 155—157 °C; ν_{max} 3500 and 1760 cm^{-1}; δ 2.30 (3H, s) and 4.67 (1H, m, H-7)] on treatment with a saturated sodium carbonate solution in

methanol. The oxidation of **1i** with chromium trioxide in acetic acid afforded cryptojaponol acetate (**1g**).[19] From the above results, the structure of compound **1b** is assigned as 7-hydroxydeoxocryptojaponol. The orientation of the hydroxy substitutent was elucidated as follows. That **1b**, **1h**, **1i**, and **1j** possess a C-7 axial proton was deduced from the larger couplings with H-6 protons, *e.g.* **1b** ($W_{1/2}$ = 16 Hz), **1h** (dd, J = 13, 6 Hz), **1i** ($W_{1/2}$ = 17 Hz), and **1j** ($W_{1/2}$ = 16 Hz). Kondo *et al.* have prepared 7β-hydroxydeoxocryptojaponol (**1b**) from cryptojaponol (**1c**) by reduction with sodium borohydride.[19] This is the first time that this compound has been isolated from a natural source.

Suginal (**2a**), mp 227 °C (dec.), has the molecular formula $C_{20}H_{26}O_3$ on the basis of elementary analysis. The ultraviolet (UV) spectrum (λ_{max} 230 and 286 nm) and IR spectrum (ν_{max} 3050, 1680, 1610, 1580, 1500 cm^{-1}) suggested the presence of the benzoyl moiety. The ^{1}H-NMR spectrum indicated the presence of two tertiary methyl groups [δ CD_3OD 1.25 and 1.29 (each 3H, s)], an isopropyl group [δ 1.26 (6H, d, J = 6.6 Hz) and 3.26 (1H, m, J = 6.6 Hz); ν_{max} 1380 and 1360 cm^{-1}], two aromatic protons [δ 7.05 and 7.59 (each 1H, s)], and an aldehyde [δ 9.60 (1H, s); ν_{max} 2760 and 1710 cm^{-1}], in addition to a hydroxyl absorption (ν_{max} 3200) in the IR spectrum. Suginal (**2a**) differs from sugiol (**10a**) only in that a tertiary methyl group is replaced by an aldehyde group. On treatment with acetic anhydride in pyridine, suginal (**2a**) afforded the monoacetate (**2b**) [mp 200—202 °C; ν_{max} 1750 cm^{-1}; δ 2.36 (3H, s)]. Sodium borohydride reduction of **2a** yielded the diol (**2c**) [mp 210—212 °C; ν_{max} 3350 cm^{-1}], which contains a primary hydroxyl [δ 3.52 and 3.76 (each 1H, d, J = 12.0 Hz)] and a secondary equatorial hydroxyl [δ 4.88 (1H, m, $W_{1/2}$ = 16 Hz)]. Compound **2c** shows no carbonyl absorption band in its IR spectrum and the signals of H-11 and H-14 were shifted upfield to δ 6.57 and 6.72, respectively. This evidence proved that the ketone in **2a** is conjugated with an aryl group. For reduction of the carbonyl group to methylene *via* the dithioketal, sugiol (**10a**) served as a model compound. When sugiol (**10a**) was allowed to react with ethanedithiol in BF_3-etherate at room temperature overnight, it gave the ethylenethioketal (**10b**) (mp 157—158 °C; in good yield) which exhibited signals at δ 3.2—3.7 (4H, m, $-SCH_2CH_2S-$) with no carbonyl absorption band in the IR spectrum. Ferruginol (**10c**) (mp 49—50 °C) was obtained when **10b** was heated at reflux in EtOH with W-2 Raney-Ni. But when **2a** was allowed to react with excess ethanedithiol in BF_3-etherate, it unexpectedly gave a monoethylenethioketal (**2d**) which showed an IR absorption band at ν_{max} 1680 cm^{-1} and ^{1}H-NMR signals at δ 5.33 (1H, s, $-CH<\begin{matrix}S-\\S-\end{matrix}$) and 3.2—3.6 (4H, m, $-SCH_2CH_2S-$) instead of an aldehyde signal. Hydrogenolysis of **2d** with W-2 Raney-Ni in refluxing EtOH gave sugiol (**10a**) in good yield. From the above results, suginal (**2a**) is a derivative of sugiol (**10a**) with an aldehyde group instead of a methyl group. According to the ^{1}H-NMR data for **2a**, the aldehyde group must be located at the C-10 or C-4 position. As the carbonyl group is axial, it will cause the signal of the axial methyl group on the same side to shift to higher field by about 0.1—0.3 due to the carbonyl anisotropic effect.[22] The C-10 CH_3 of agathalic acid (**16**)[23] shows an abnormally high-field ^{1}H-NMR signal of δ 0.58.[23] The ^{1}H-NMR signals of C-10 CH_3 of sugiol acetate (**10d**), ferruginol (**10c**), ferruginol acetate (**10e**),[24] and compound **17**[25] appear at δ 1.20, 1.13, 1.17, and 1.07, respectively. The methyl groups of suginal (**2a**) are all at lower field than δ 1.26, so the location of the aldehyde group at C-10 can be excluded. Thus we conclude that the aldehyde group is positioned at C-4 in α-equatorial orientation as shown in the formula (**2a**).

Detetrahydroconidendrin (**3a**), mp 254 °C (dec.), exhibited IR absorption bands at 3300 (–OH), 1750 (lactone), 3030, 1620 and 1515 cm^{-1} (aromatic absorption). The formula $C_{20}H_{16}O_6$ followed from the mass spectrum (M^+ 352). The UV spectrum in methanol indicated the presence of an extended naphthalenic chromophore (λ_{max} 258 and 322 nm). In addition to the ^{1}H-NMR signals at δ CD_3OD 3.80 and 4.02 (each 3H, s) due to the methoxyl groups, detetrahydroconidendrin (**3a**) showed three aromatic singlets at 7.15, 7.44 and 8.25 (each 1H, s), three other aromatic protons at 6.80 (1H, d, J = 8.1 Hz), 6.94 (1H, s), and 6.98 (1H, d, J = 8.1 Hz) and two methylene protons at 5.27 (s). Treatment of **3a** with acetic anhydride in pyridine afforded the diacetate (**3b**) [mp 226—227 °C: ν_{max} 1750 cm^{-1}, no hydroxyl absorption; δ 2.34 and 2.38 (each 3H, s)] in which the signal of H-8 is shifted downfield from 7.15 to 7.48 and that of H-5′ from 6.98 to 7.22. Based on the above data, detetrahydroconidendrin (**3a**) is proposed to be a phenyl naphthalene type lignan with a γ-lactone fused on naphthalene. The signal of the aromatic H-4 at δ 8.25 indicated that it was strongly deshielded by the lactone carbonyl, which must be located at C-3a. Helioxanthin (**18**)[26] and compound **3c**[27] show signals at δ 8.38 and 8.30, respectively, due to H-4. In contrast, taiwanin C (**19**) exhibits the corresponding proton signal at δ 7.71.[28] The methylene signal appears at higher field than δ 5.33,[29] reinforcing the structural assignment as in **3a**. Further evidence to confirm the identification of **3a** as detetrahydroconidendrin is that diacetate (**4c**), prepared from α-conidendrin (**4d**), was dehydrogenated by dichlorodicyanobenzoquinone in refluxing benzene to yield a product which was identical with **3b**. Furthermore, dimethyldetetrahydroconidendrin (**3c**) prepared from **3a** by treatment with diazomethane in methanol gave physical data in agreement with those in the literature.[27]

Formosanol (**4a**), mp 188—189 °C, exhibits IR absorption bands at ν_{max} 3440 (OH), 1610, 1580, and 1510 cm^{-1}

TABLE I. ^{13}C-NMR Data (δ-Values) for Methyl α-Conidendral Acetate (**4g**) and Formosanol Acetate (**4e**)

C	4g	4e	C	4g	4e
1	49.1 d	46.1 d	8a	131.3 s	131.4 s
2	49.5 d	50.8 d	1′	142.6 s	142.8 s
2a	70.9 t	71.9 t	2′	112.0 d	111.9 d
3	47.6 d	45.7 d	3′	151.2 s	151.0 s
3a	109.9 d	104.6 d	4′	138.6 s	138.4 s
4	31.9 t	29.5 t	5′	122.8 d	122.6 d
4a	134.9 s	135.2 s	6′	120.6 d	120.6 d
5	112.8 d	112.7 d	$ArOC\underline{H}_3$	55.7 q	55.7 q
6	149.5 s	149.2 s	$3a\text{-}OC\underline{H}_3$	56.4 q	54.7 q
7	138.0 s	137.6 s	$\underline{C}H_3CO-$	20.5 q	20.6 q
8	123.5 d	123.2 d	$CH_3\underline{C}O-$	168.6 s	168.6 s

Run in $CDCl_3$ at 100 MHz with TMS as an internal standard; s, singlet; d, doublet; t, triplet; q, quartet.

(aromatic absorption). The formula $C_{21}H_{24}O_6$ followed from elementary analysis. Compound **4a** shows ^{1}H-NMR signals at δ 3.38, 3.80 and 3.85 (each 3H, s), 3.00 and 3.68 (each 2H, m, H-4, H-2a), 4.98 (1H, d, J=4.4 Hz, H-3a), 6.34 and 6.62 (each 1H, s, H-8, H-5), 6.55 (1H, d, J=1.5 Hz, H-2′), 6.65 (1H, dd, J=7.8, 1.5 Hz, H-6′), and 6.82 (1H, d, J=7.8 Hz, H-5′). Treatment of formosanol (**4a**) with acetic anhydride in pyridine afforded the diacetate (**4e**) [mp 98—99 °C; ν_{max} 1750 cm^{-1}, no hydroxyl absorption; δ 2.20 and 2.24 (each 3H, s)]. The result indicated that formosanol (**4a**) contains two aromatic hydroxyl groups. Further proof is provided by the fact that in the reaction with dimethyl sulfate and potassium carbonate in refluxing acetone, formosanol (**4a**) gave the pentamethoxy derivative (**4f**) [mp 67—68 °C; no hydroxy absorption; δ 3.38, 3.58, 3.79, 3.86, and 3.88 (each 3H, s)]. Comparison of ^{1}H-NMR and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of formosanol acetate (**4e**) and methyl α-condiendral acetate (**4g**)[7] (Table I) shows that formosanol is an isomer of methyl α-conidendral. Further support for this result is provided by the fact that formosanol diacetate (**4e**), on reaction with BF_3-etherate and *m*-chloroperbenzoic acid,[30] was converted to α-conidendrin diacetate (**4c**), which was also obtained from methyl α-conidendral acetate by similar oxidation.[7] From the above evidence, formosanol and methyl α-conidendral are concluded to be epimers with different relative configurations at C-3a. Cheng *et al.* have isolated tsugacetal[31] (from *Tsuga chinesis*), which was identical with formosanol,[32] and showed by X-ray analysis that its structure is **4a**.[31] Therefore the structures of formosanol and methyl α-conidendral must be **4a** and **4b**, respectively.

Junipediol (**5a**), mp 170—171 °C, has the molecular formula $C_{15}H_{26}O_2$ on the basis of elementary analysis. The IR spectrum revealed the presence of secondary alcohol (ν_{max} 3470, 3250, 1060, and 1040 cm^{-1}) and cyclopropane (ν_{max} 3020 cm^{-1}) absorptions. Junipediol (**5a**) showed ^{1}H-NMR signals due to a triply substituted cyclopropane [δ CD_3OD 0.14—0.63 (3H, m)], four tertiary methyl groups

Table II. Crystal Data

Formula	$C_{15}O_2H_{26}\cdot H_2O$
Mol. Wt. (g mol^{-1})	256
Crystal size (mm)	0.1×0.3×0.55
Space group	$P\,2_1/c$
a	15.343 (2)
b Å	6.308 (1)
c	16.726 (2)
β	109.88 (1)
Vol (Å^3)	1522.34
Z	4
D_c (g·cm^{-3})	1.12
F_{ooo}	568
Radiation	Mo K_α (λ=0.7107 Å)
Scan speed (deg/min)	20/3—20/20
2θ range (Mo K_α)	2—50°
$\theta/2\theta$ scan parameter	2 (0.8+0.35 tan θ)
Abs. coeff. (cm^{-1})	0.71
Total reflections	2984
Observed reflections (>2σ)	1656
Quadrant collected	$hk\pm l$
R, R_w	0.086, 0.083
S	5.56

Table III. Atomic Parameters x, y, z and B_{iso} of $C_{15}O_2H_{26}\cdot H_2O$

	x	y	z	B_{iso}
C1	0.7060 (5)	0.2413 (12)	0.4023 (4)	2.9 (3)
C2	0.6736 (5)	0.0861 (12)	0.3280 (4)	3.1 (3)
C3	0.7363 (5)	0.0287 (12)	0.2798 (4)	3.1 (4)
C4	0.8321 (4)	0.1280 (12)	0.3115 (4)	3.1 (4)
C5	0.8934 (5)	0.0198 (13)	0.3929 (4)	4.0 (4)
C6	0.8436 (5)	−0.0218 (13)	0.4572 (4)	3.4 (4)
C7	0.7914 (5)	0.1671 (12)	0.4777 (4)	3.1 (4)
C8	0.7473 (5)	0.0991 (13)	0.5445 (4)	3.7 (4)
C9	0.6720 (5)	0.2608 (15)	0.5364 (4)	4.8 (5)
C10	0.6274 (5)	0.2990 (13)	0.4409 (5)	3.7 (4)
C11	0.6535 (5)	0.1620 (13)	0.2390 (4)	3.7 (4)
C12	0.7321 (6)	−0.2044 (14)	0.2472 (5)	4.7 (5)
O13	0.8796 (3)	0.1046 (8)	0.2503 (3)	3.5 (3)
C14	0.8587 (5)	0.3555 (14)	0.5126 (5)	5.1 (5)
O15	0.8092 (4)	0.0945 (9)	0.6301 (3)	4.7 (3)
C16	0.5387 (5)	0.1640 (14)	0.4057 (5)	4.6 (5)
C17	0.6006 (6)	0.5346 (15)	0.4229 (5)	5.6 (5)
O21	0.9298 (3)	−0.2255 (9)	0.6834 (4)	6.0 (3)

Estimated standard deviations (E.S.Ds.) refer to the last digit printed.

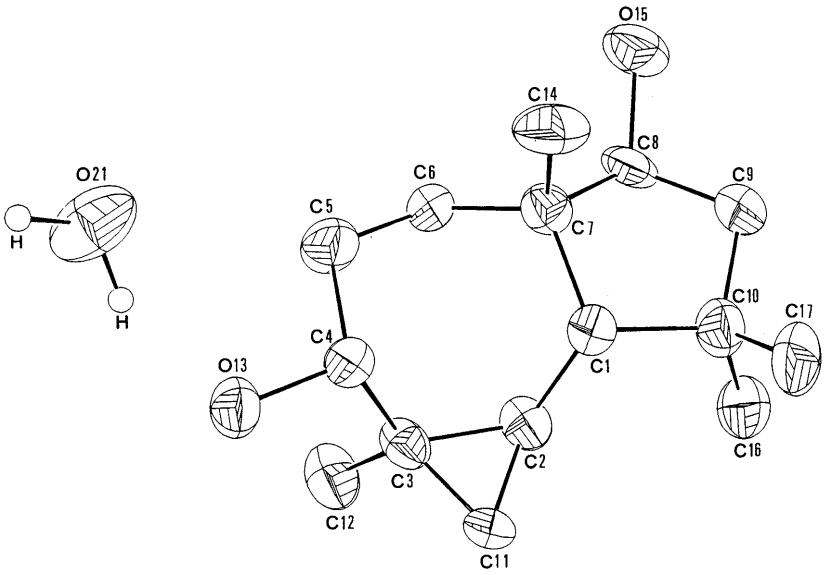

Fig. 1

TABLE IV. Bond Lengths and Angles of $C_{15}O_2H_{26}\cdot H_2O$

Bond lengths		Bond angles			
C(1)–C(2)	1.527 (10)	C(2)–C(1)–C(7)	114.9 (6)	C(1)–C(7)–C(6)	114.3 (6)
C(1)–C(7)	1.550 (9)	C(2)–C(1)–C(10)	113.2 (6)	C(1)–C(7)–C(8)	102.3 (5)
C(1)–C(10)	1.590 (10)	C(7)–C(1)–C(10)	106.7 (5)	C(1)–C(7)–C(14)	110.2 (6)
C(2)–C(3)	1.495 (9)	C(1)–C(2)–C(3)	120.2 (6)	C(6)–C(7)–C(8)	109.5 (6)
C(2)–C(11)	1.493 (10)	C(1)–C(2)–C(11)	120.4 (6)	C(6)–C(7)–C(14)	110.3 (6)
C(3)–C(4)	1.517 (10)	C(3)–C(2)–C(11)	59.4 (5)	C(8)–C(7)–C(14)	109.8 (6)
C(3)–C(11)	1.482 (10)	C(2)–C(3)–C(4)	115.8 (6)	C(7)–C(8)–C(9)	104.8 (6)
C(3)–C(12)	1.562 (11)	C(2)–C(3)–C(11)	60.2 (5)	C(7)–C(8)–O(15)	115.1 (6)
C(4)–C(5)	1.528 (10)	C(2)–C(3)–C(12)	117.3 (6)	C(9)–C(8)–O(15)	109.4 (6)
C(4)–O(13)	1.453 (8)	C(4)–C(3)–C(11)	120.2 (7)	C(8)–C(9)–C(10)	104.9 (6)
C(5)–C(6)	1.539 (10)	C(4)–C(3)–C(12)	115.5 (6)	C(1)–C(10)–C(9)	104.8 (6)
C(6)–C(7)	1.538 (10)	C(11)–C(3)–C(12)	116.5 (6)	C(1)–C(10)–C(16)	114.3 (6)
C(7)–C(8)	1.552 (10)	C(3)–C(4)–C(5)	110.9 (6)	C(1)–C(10)–C(17)	109.3 (6)
C(7)–C(14)	1.552 (11)	C(3)–C(4)–O (13)	111.7 (5)	C(9)–C(10)–C(16)	109.6 (6)
C(8)–C(9)	1.511 (11)	C(5)–C(4)–O(13)	106.1 (5)	C(9)–C(10)–C(17)	110.5 (7)
C(8)–O(15)	1.423 (8)	C(4)–C(5)–C(6)	113.4 (6)	C(16)–C(10)–C(17)	108.3 (7)
C(9)–C(10)	1.528 (10)	C(5)–C(6)–C(7)	116.4 (6)	C(2)–C(11)–C(3)	60.3 (5)
C(10)–C(16)	1.542 (11)				
C(10)–C(17)	1.544 (12)				

[δ 0.88, 1.00, 1.05 and 1.12 (each 3H, s)], and two protons on carbon bearing oxygen [δ 3.30 (1H, dd, $J=10.5$, 5.9 Hz) and 3.70 (1H, dd, $J=10.0$, 8.0 Hz)]. Acetylation of junipediol (**5a**) yielded the diacetate (**5b**) (mp 94—95 °C), which exhibited two acetate absorption signals [ν_{max} 1735 cm^{-1}; δ 1.95 and 1.98 (each 3H, s)] and the signals of protons attached to carbons bearing a hydroxyl group were shifted downfield to δ 4.36 (1H, dd, $J=10.6$, 6.6 Hz) and 4.71 (1H, dd, $J=10.6$, 7.1 Hz). The relative configuration and the structure of junipediol (**5a**) were determined by X-ray diffraction analysis. It has a novel skeleton which has not previously been isolated from a natural source.

Compound **5a** crystallized in monoclinic space group $P2_1/C$, with unit cell dimensions: $a=15.343(2)$, $b=6.308(1)$, $c=16.726(2)$, $\beta=109.88(1)°$, $Z=4$. Intensity data were measured on a CAD4 diffractometer at room temperature. The other experimental details are given in Table II. The structure was solved by the direct method. The molecule consists of a three-membered ring and a five-membered ring, both edge shared with a seven-membered ring. All the C–C, C–O bond lengths are normal. The molecular structure is depicted in Fig. 1. Fractional atomic coordinates are given in Table III. Bond lengths and bond angles are listed in Table IV. There are four water molecules in the unit cell. The two hydroxyl groups (O13; O15) of the molecule and a water (O21) molecule are hydrogen-bonded to each other intermolecularly. The corresponding O···O distances are 2.708(7), 2.678(7) and 2.856(7) Å for O13···O15; O15···O21 and O21···O13, respectively. Therefore, all the molecules are strongly hydrogen-bonded to each other throughout the crystal.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-180 at room temperature. IR spectra were recorded on a Jasco IRA-I spectrometer. ^1H- and ^{13}C-NMR spectra were run on a Varian T-60 at 60 MHz and JEOL JNM-FX-100 at 100 MHz with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ values and coupling constants (J) are given in hertz (Hz). Electron impact-mass spectra (EI-MS) were taken on a Hitachi RMS-4 and X-ray analysis was done on an Enraf Nonius 586 apparatus.

Extraction and Isolation The heartwood of *Juniperus formoana* (21 kg) was cut into thin pieces, which were extracted with hexane (60 l) four times at room temperature to give hexane extracts and a residue. The hexane extract was partitioned with hexane (2 l) and 90% aqueous methanol (2 l). The methanol layer was evaporated under reduced pressure and afforded a brown extract, which was dissolved in ether. The ether solution was subsequently extracted with 5% $NaHCO_3$, 3% Na_2CO_3, and 2% NaOH aqueous solution to give bicarbonate-soluble (20 g), carbonate-soluble (17 g), hydroxide-soluble (0.7 g), and neutral fractions (200 g), respectively. Every fraction was repeatedly chromatographed on silica gel to give the following products: 7α-methoxydeoxocryptojaponol (**1a**) (3.1 g), 7β-hydroxydeoxocryptojaponol (**1b**) (2.5 g), cryptojaponol (**1c**) (3.5 g), α-cedrol (**6a**) (51 g), sugiol (**10a**) (3.0 g), and β-sitosterol (4.8 g).

The residue was subsequently extracted with acetone and the acetone extract was also separated into four fractions in the same manner as described above. These fractions were repeatedly chromatographed on silica gel to give the following products: **1a** (0.8 g), **1c** (0.2 g), suginal (**2a**) (85 mg), detetrahydroconidendrin (**3a**) (90 mg), formosanol (**4a**) (120 mg), methyl α-conidendral (**4b**) (0.2 g), junipediol (**5a**) (40 mg), α-cedrol (**6a**) (10.5 g), 4-ketocedrol (**6b**) (0.8 g), 3β-hydroxycedrol (**6c**) (0.4 g), isocedrolic acid (**6d**) (0.1 g), δ-cadinol (**7**) (0.3 g), cadin-8-en-10-ol (**8**) (0.1 g), clovandiol (**9**) (30 mg), sugiol (**10a**) (0.5 g), Δ^5-dehydrosugiol (**11**) (0.1 g), totarol (**12a**) (90 mg), 7-oxototarol (**12b**) (80 mg), and emodin (**13**) (35 mg). The physical characteristics of the pure compounds are as follows.

7α-Methoxydeoxocryptojaponol (**1a**): mp 160—161 °C, $[\alpha]_D^{25}$ +21.8° ($c=1.0$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400, 3030, 1610, 1500, 1420, 1375, 1360, 1235, 1080, 1060, 1020, 870, 840, 750. *Anal.* Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.01; H, 9.92.

7β-Hydroxydeoxocryptojaponol (**1b**): mp 168—170 °C, $[\alpha]_D^{23}$ +17.5° ($c=1.0$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3540, 3240, 3050, 1600, 1500, 1410, 1375, 1360, 1300, 1240, 1160, 1110, 1040, 1020, 990, 880, 820. *Anal.* Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.99; H, 9.61.

Cryptojaponol (**1d**)[6]: mp 205—206 °C. IR ν_{max}^{KBr} cm^{-1}: 3400, 3030, 1700, 1600, 1610, 1480, 1340, 1265, 1220, 1160, 1110, 1030, 1010, 880. ^1H-NMR ($CDCl_3$) δ: 0.94, 0.96, 1.40 (each, 3H, s), 1.21 and 1.28 (each 3H, d, $J=7.0$ Hz), 3.20 (1H, m, $J=7.0$ Hz), 6.17 (1H, s, –OH), and 7.61 (each 1H, s).

Suginal (**2a**): mp 227 °C (dec.), $[\alpha]_D^{15}$ −100.5° ($c=1.0$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3200, 2760, 1710, 1670, 1610, 1580, 1500, 1380, 1360, 1285, 1180, 1060, 1000, 770, 630. UV λ_{max}^{MeOH} nm (log ε): 203 (4.21), 286 (4.10). *Anal.* Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.51; H, 8.27.

Detetrahydroconidendrin (**3a**) mp 254 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3300, 3030, 1750, 1735, 1620, 1515, 1495, 1350, 1280, 1220, 1190, 1040, 775. UV λ_{max}^{MeOH} nm (log ε) 258 (4.75), 322 (4.19). MS m/z (%): 352 (66, M^+), 335 (18), 324 (33), 115 (48), 113 (60), 102 (79), 89 (46), 138 (98), 124 (100), 104 (46), 96 (75). *Anal.* Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.09; H, 4.50.

Formosanol (**4a**): mp 188—189 °C, $[\alpha]_D^{23}$ −81.3° ($c=1.0$, $CHCl_3$), IR

ν_{max}^{KBr} cm^{-1}: 3440, 3040, 1610, 1580, 1510, 1275, 1260, 1120, 1000, 915, 885, 770, 670. MS *m/z* (%): 372 (M^+, 16), 340 (100), 310 (21), 293 (22), 279 (36), 271 (13), 216 (45), 188 (30), 175 (38), 162 (26), 137 (87). *Anal.* Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.61; H, 6.43.

Methyl α-Conidendral (**4b**)[7]: mp 225—227 °C. IR ν_{max}^{KBr} cm^{-1}: 3450, 3080, 1610, 1590, 1510, 1280, 1090, 985, 920, 785, 765. ^{1}H-NMR ($CDCl_3$) δ: 2.95 (2H, m, H-4), 3.49, 3.80, and 3.86 (each 3H, s), 3.70 (2H, m, H-2a), 4.78 (1H, d, J=5.8 Hz, H-3a), 6.31, 6.64 (each 1H, s), 6.56 (1H, br s), 6.66 and 6.78 (each 1H, d, J=8.0 Hz).

Junipediol (**5a**): mp 170—171 °C, $[\alpha]_D^{20}$ +68° (c=1.0, CH_3OH). IR ν_{max}^{KBr} cm^{-1}: 3470, 3250, 3020, 1380, 1365, 1350, 1060, 1040, 1010, 880, 625. *Anal.* Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.47; H, 10.97.

β-Sitosterol: mp 137—138 °C. IR ν_{max}^{KBr} cm^{-1}: 3420, 1660, 1380, 1360, 1240, 1050, 1020, 840, 810. ^{1}H-NMR ($CDCl_3$) δ: 0.66 and 1.01 (each 3H, s), 0.83 (3H, d, J=7.2 Hz), 0.79, 0.81, and 0.90 (each 3H, d, J=6.6 Hz), 3.50 (1H, m), 5.40 (1H, br s).

α-Cedrol (**6a**)[1]: mp 85—86 °C. IR ν_{max}^{KBr} cm^{-1}: 3300, 1240, 1145, 1060, 980, 940. ^{1}H-NMR ($CDCl_3$) δ: 0.83 (3H, d, J=6.6 Hz), 0.98, 1.23 and 1.30 (each 3H, s).

4-Ketocedrol (**6b**)[1,8]: mp 129—130 °C. IR ν_{max}^{KBr} cm^{-1}: 3460, 1730, 1160, 1130, 940, 630. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, d, J=6.6 Hz), 0.97, 1.25, 1.38 (each 3H, s).

3β-Hydroxycedrol (**6c**)[1,9]: mp 164—165 °C. IR ν_{max}^{KBr} cm^{-1}: 3300, 1390, 1380, 1120, 1100, 1085, 1045, 980, 940. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, d, J=8.0 Hz), 1.01, 1.28 and 1.35 (each 3H, s), 3.67 (1H, m, $W_{1/2}$=24 Hz).

Isocedrolic Acid (**6d**)[1,10]: mp 259—261 °C. IR ν_{max}^{KBr} cm^{-1}: 3320, 3100—2500, 1670, 1275, 1190, 1140, 1110, 920, 700. ^{1}H-NMR (DMSO-d_6) δ: 0.96, 1.15 and 1.26 (each 3H, s).

δ-Cadinol (**7**)[11]: mp 137—138 °C. IR ν_{max}^{KBr} cm^{-1}: 3320, 1370, 1300, 1220, 1140, 1060, 880. ^{1}H-NMR ($CDCl_3$) δ: 0.82 and 0.88 (each 3H, d, J=6.8 Hz), 1.29 (3H, s), 1.65 (3H, br s), 5.51 (1H, d, J=5.5 Hz).

Cadin-8-en-10-ol (**8**)[12]: mp 75—76 °C. IR ν_{max}^{KBr} cm^{-1}: 3350, 3040, 1680, 1385, 1365, 1300, 1260, 1210, 1080, 1030, 920, 900, 860, 840. ^{1}H-NMR ($CDCl_3$) δ: 0.80 and 0.95 (each 3H, d, J=6.7 Hz), 0.87 (3H, d, J=7.1 Hz), 1.71 (3H, br s), 5.47 (1H, br s).

Clovandiol (**9**)[13]: mp 151—152 °C. IR ν_{max}^{KBr} cm^{-1}: 3400, 3320, 1090, 1070, 1055, 1010, 980, 960, 940, 790, 740. ^{1}H-NMR ($CDCl_3$) δ: 0.86, 0.96, and 1.03 (each 3H, s), 2.28 (2H, br s, –OH), 3.32 (1H, br s, $W_{1/2}$=7.0 Hz), 3.77 (1H, m, $W_{1/2}$=21 Hz). Clovandiol diacetate (**9b**): mp 97—98 °C. IR ν_{max}^{KBr} cm^{-1}: 1725, 1230, 1050, 1020, 970, 915; ^{1}H-NMR ($CDCl_3$) δ: 0.84, 0.92, 1.05, 2.04 and 2.05 (each 3H, s), 4.50 (1H, br s, $W_{1/2}$=7.0 Hz), 4.82 (1H, dd, J=8.0, 6.0 Hz).

Sugiol (**10a**)[14]: mp 278 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3100, 1650, 1580, 1560, 1310, 1270, 1180, 990, 870, 775, 660. ^{1}H-NMR (C_5D_5N) δ: 0.80, 0.85 and 1.12 (each 3H, s), 1.33 (6H, d, J=7.0 Hz), 2.70 (2H, m), 3.56 (1H, m), 5.20 (1H, br s, –OH), 7.08 and 8.30 (each 1H, s). Sugiol acetate (**10d**); mp 166—167 °C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1675, 1505, 1570, 1500, 1460, 1380. ^{1}H-NMR ($CDCl_3$) δ: 0.91, 0.95, 1.30, and 2.32 (each 3H, s), 1.25 (6H, d, J=7.0 Hz), 6.98 and 7.98 (each 1H, s).

Δ^5-Dehydrosugiol (**11**)[15]: mp 274 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3100, 1640, 1610, 1500, 1380, 1340, 1310, 1260, 790, 775. ^{1}H-NMR (C_5D_5N) δ: 1.12, 1.16 and 1.40 (each 3H, s), 1.36 (6H, d, J=7.0 Hz), 6.58, 7.34 and 8.46 (each 1H, s).

Totarol (**12a**)[16]: mp 126—128 °C. IR ν_{max}^{KBr} cm^{-1}: 3510, 3030, 1580, 1480, 1280, 1175, 1115, 1090, 970, 910, 815. ^{1}H-NMR ($CDCl_3$) δ: 0.98, 0.98 and 1.20 (each 3H, s), 1.40 (6H, d, J=7.1 Hz), 3.26 (1H, m, J=7.1 Hz), 6.56 and 7.10 (each 1H, d, J=8.0 Hz).

7-Oxototarol (**12b**)[17]: mp 194—196 °C. IR ν_{max}^{KBr} cm^{-1}: 3400, 3020, 1675, 1595, 1580, 1480, 1275, 1175, 1100, 1075, 810. ^{1}H-NMR ($CDCl_3$) δ: 0.88, 1.08 and 1.16 (each 3H, s), 1.34 (6H, d, J=7.1 Hz), 3.24 (1H, m, J=7.1 Hz), 6.54 and 6.90 (each 1H, d, J=8.5 Hz).

Emodin (**13**)[18]: mp 254 °C. UV λ_{max}^{EtOH} nm: 252, 265, 289, 437. IR ν_{max}^{KBr} cm^{-1}: 3350, 3200—2700, 1630, 1580, 1555, 1480, 1270, 1215, 1165, 1105, 760. ^{1}H-NMR (CD_3OD) δ: 2.44 (3H, s), 6.56 and 7.19 (each 1H, d, J=2.5 Hz), 7.16 and 7.57 (each 1H, d, J=1.5 Hz).

Acetylation of 1a to 1e 7α-Methoxydeoxycryptojaponol (**1a**) (60 mg) was allowed to react with Ac_2O (0.5 ml) and pyridine (0.5 ml) at room temperature for 7 d. Usual work-up gave the monoacetate **1e** (60 mg): mp 95—96 °C. IR ν_{max}^{KBr} cm^{-1}: 1745, 1300, 1240, 1220, 1080, 1020, 980, 890, 840, 750. ^{1}H-NMR ($CDCl_3$) δ: 0.95, 0.97, 1.19 and 2.26 (each 3H, s), 1.25 (6H, d, J=6.5 Hz), 3.23 (1H, m, J=6.5 Hz), 3.30 and 3.69 (each 3H, s), 4.06 (1H, br s, $W_{1/2}$=4.5 Hz), 6.70 (1H, s).

Catalytic Hydrogenation of 1e with Pd–C Compound **1e** (54 mg) was dissolved in 5 ml of MeOH, then 10 mg of 10% Pd–C previously suspended in 5 ml of MeOH was added and the mixture was saturated with H_2. After 12 h, the catalyst was removed by filtration and washed several times with MeOH. After purification, the combined filtrate and washing yielded a product (**1f**) (49 mg) [mp 155—157 °C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1380, 1235, 1035, 905, 785. ^{1}H-NMR ($CDCl_3$) δ: 0.93, 0.95, 1.24, 2.27 and 3.75 (each 3H, s), 2.80 (2H, m), 6.85 (1H, s)] which was identical with deoxocryptojaponol acetate.[19]

Oxidation 1f to Cryptojaponol Acetate (1g) A solution of 90 mg of chromium trioxide in 2 ml of acetic acid containing a few drops of water was added to a solution of 90 mg of **1f** in 1 ml of acetic acid. The mixture was left at room temperature for 10 h, poured into water and extracted with ether. Usual work-up gave cryptojaponol acetate (**1g**) (mp 167—169 °C) (45 mg).[19]

Catalytic Hydrogenation of 1a with Pd–C to Deoxocryptojaponol (1d) 7α-Methoxydeoxocryptojaponol (**1a**) (70 mg) was hydrogenated with 10% Pd–C (20 mg) in methanol solution in the same way as mentioned above to yield deoxocryptojaponol (**1d**) (mp 93—95 °C) (60 mg).[19]

Elimination of Methanol from 1a with Ag_2O Silver oxide (25 mg) was added to a solution of **1a** (80 mg) and methyl iodide (100 mg) in 5 ml of DMF. The reaction mixture was stirred at room temperature for 16 h. After purification on silica gel it yielded **14** (65 mg) [mp 102—104 °C. IR ν_{max}^{KBr} cm^{-1}: 3050, 1620, 1500, 1300, 1250, 1200, 1080, 1030, 870. ^{1}H-NMR ($CDCl_3$) δ: 0.94, 1.00, 1.10 and 3.73 (each 3H, s), 1.18 and 1.20 (each 3H, d, J=6.5 Hz), 2.20 (1H, dd, J=4.1, 3.2 Hz), 3.10 (1H, m, J=6.5 Hz), 5.90 (1H, dd, J=10.0, 4.1 Hz), 6.30 (1H, dd, J=10.0, 3.2 Hz), 6.44 (1H, s)]. Catalytic hydrogenation of **14** with 10% Pd–C in methanol yielded **1d** quantitatively.

Oxidation of 1a with *m*-Chloroperbenzoic Acid *m*-Chloroperbenzoic acid (100 mg) and **1a** (75 mg) were dissolved in 5 ml of CH_2Cl_2 and were kept at room temperature for36 h. Then 25 ml of Na_2SO_3 (100 mg) aqueous solution was poured into the reaction mixture and the whole was stirred for 1 d. The product was extracted with CH_2Cl_2, then purified on silica gel to give a red product (40 mg) [mp 167—168 °C. IR ν_{max}^{KBr} cm^{-1}: 3300, 3080, 1660, 1630, 1600, 1550, 1170, 918, 808, 772, 760, 718. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H, s), 1.05 (6H, s), 1.21 (6H, d, J=7.5 Hz), 3.13 (1H, quintet, J=7.5 Hz), 6.60 and 6.90 (each 1H, dd, J=10.5, 3.0 Hz)] which was identical with 6,7-dehydroroyleanone (**15a**).[21]

Elimination of Methanol from 1a by *m*-Chlorobenzoic Acid *m*-Chlorobenzoic acid (70 mg) and **1a** (30 mg) were dissolved in 5 ml of CH_2Cl_2 and kept at room temperature for 30 h. After purification, compound **14** (40 mg) was isolated.

Acetylation of 1b with Acetic Anhydride and Pyridine Compound **1b** (80 mg) was treated with Ac_2O (0.5 ml) and pyridine (0.5 ml) at room temperature overnight to give the monoacetate (**1h**) (75 mg) [mp 116—118 °C. IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1600, 1480, 1230, 1030, 950. ^{1}H-NMR ($CDCl_3$) δ: 0.92, 0.97, 1.35, 2.13, and 3.69 (each 3H, s), 1.12 and 1.15 (each 3H, d, J=6.5 Hz), 3.13 (1H, m, J=6.5 Hz), 5.90 (1H, dd, J=13.0, 6.0 Hz), 6.00 (1H, s, –OH), 6.47 (1H, s)]. Compound (**1h**) (65 mg) and Ac_2O (0.5 ml) were heated at 75 °C for 24 h in pyridine (1 ml) solution. Usual work-up gave the diacetate (**1i**) (63 mg) [mp 122—124 °C. IR ν_{max}^{KBr} cm^{-1}: 1760, 1735, 1240, 1200, 1020, 890, 800. ^{1}H-NMR ($CDCl_3$) δ: 0.98, 1.01, 1.30, 2.06, 2.24, and 3.68 (each 3H, s), 1.14 (6H, d, J=6.4 Hz), 3.15 (1H, m, J=6.4 Hz), 5.89 (1H, m, $W_{1/2}$=17 Hz), 6.90 (1H, s)].

Partial Saponification of 1i with Na_2CO_3 in MeOH The diacetate (**1i**) (50 mg) was added to 5 ml of saturated Na_2CO_3 methanol solution for 3 h at room temperature. The reaction mixture was poured into 50 ml of water, then extracted with ethyl acetate. The extract was purified to yield the monoacetate (**1j**) (30 mg) [mp 155—157 °C. IR ν_{max}^{KBr} cm^{-1}: 3500, 1760, 1200, 1025, 880. ^{1}H-NMR ($CDCl_3$) δ: 0.98, 1.00, 1.30, 2.30, and 3.68 (each 3H, s), 1.16 (6H, d, J=6.5 Hz), 3.15 (1H, m, J=6.5 Hz), 4.67 (1H, m, $W_{1/2}$=16 Hz), 7.30 (1H, s)].

Oxidation of 1j with Chromium Trioxide Compound **1j** (28 mg) and chromium trioxide (70 mg) dissolved in a solution of 3 ml of acetic acid and 0.5 ml of water were stirred at room temperature. After 6 h, the reaction mixture was poured into 50 ml of water then extracted with CH_2Cl_2 four times. Usual work-up gave a product (15 mg) (mp 167—168 °C) which was identical with cryptojaponol acetate (**1g**).[19]

Acetylation of Suginal (2a) When treated by a usual method, suginal (**2a**) (30 mg) gave suginal acetate (**2b**) (28 mg) [mp 200—202 °C. IR ν_{max}^{KBr} cm^{-1}: 3040, 1750, 1710, 1680, 1605, 1580, 1380, 1365, 1250, 1175, 1050, 760, 640. ^{1}H-NMR ($CDCl_3$) δ: 1.23, 1.29 and 2.36 (each 3H, s), 1.26 (6H, d, J=6.2 Hz), 3.10 (2H, m, J=6.2 Hz), 7.22, 7.75 and 9.84 (each 1H, s)].

Sodium Borohydride Reduction of Suginal (2a) An excess of sodium borohydride was added in small portions to a solution of suginal (**2a**)

(15 mg) in 5 ml of EtOH and the mixture was left to stand for 4 h. The reaction mixture was poured into an excess of water (50 ml) and extracted with ethyl acetate four times. The ethyl acetate extract was subjected to chromatography on silica gel to give the diol (**2c**) (9 mg) [mp 210—212 °C. IR ν_{max}^{KBr} cm^{-1}: 3350, 3040, 1615, 1580, 1500, 1185, 1090, 1060, 1015, 990, 900, 760. ^{1}H-NMR ($CDCl_3$) δ: 1.03 and 1.22 (each 3H, s), 1.21 and 1.23 (each 3H, d, J=6.6 Hz), 3.13 (1H, m, J=6.6 Hz), 3.52 and 3.76 (each 1H, d, J=12.0 Hz), 4.88 (1H, m, $W_{1/2}$=16 Hz), 6.57 and 6.72 (each 1H, s)].

The Ethylenethioketal (10b) from Sugiol (10a) Ethanedithiol (50 mg) and BF_3–etherate (1 ml) were added to a solution of **10a** (60 mg) in dry $CHCl_3$ (5 ml) at 0 °C for 2 h. Then the mixture was poured into a little ice-water and extracted with $CHCl_3$. The organic layer was purified on silica gel to give the ethylenethioketal (**10b**) (65 mg) [mp 157—158 °C. IR ν_{max}^{KBr} cm^{-1}: 3530, 1615, 1575, 1500, 1405, 1265, 1060, 1000, 890, 845, 765, 725, 675. ^{1}H-NMR ($CDCl_3$) δ: 0.90, 0.97 and 1.21 (each 3H, s), 1.24 and 1.26 (each 3H, d, J=7.1 Hz), 3.10 (1H, m, J=7.1 Hz), 3.2—3.7 (4H, m), 4.74 (1H, br s, –OH), 6.48 and 7.60 (each 1H, s)].

Reduction of the Ethylenethioketal (10b) with Raney-Ni Compound **10b** (50 mg) was treated with a suspension of Raney-Ni (W-2, 2 g) in absolute ethanol (30 mg) under reflux for 10 h. After purification, it gave ferruginol (**10c**) (mp 49—50 °C) (26 mg).[33]

The Monoethylenethioketal (2d) from Suginal (2a) Under similar conditions to those mentioned above, suginal (**2a**) (30 mg) gave the monoethylenethioketal (**2d**) (32 mg) [amorphous solid. IR ν_{max}^{KBr} cm^{-1}: 3400, 3050, 1680, 1610, 1575, 1410, 1270, 1170, 995, 750. ^{1}H-NMR ($CDCl_3$) δ: 1.03 and 1.23 (each 3H, s), 1.26 (6H, d, J=6.6 Hz), 3.10 (1H, m, J=6.6 Hz), 3.2—3.6 (4H, m, $-SCH_2CH_2S-$), 5.33 (1H, s, –SCHS–), 6.74 and 7.74 (each 1H, s).

Reduction of the Monoethylenethioketal (2d) with Raney-Ni Reduction of the monoethyleneketal (**2d**) (30 mg) with Raney-Ni in refluxing dry ethanol gave sugiol (**10a**)[33] (14 mg) after work-up as described above.

Acetylation of Detetrahydroconidendrin (3a) Compound **3a** (65 mg) was treated with AC_2O and pyridine as usual to yield the diacetate (**3b**) (65 mg) [mp 226—227 °C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1620, 1600, 1510, 1265, 1220, 1155, 1120, 1030, 928, 845, 775. ^{1}H-NMR ($CDCl_3$) δ: 2.34, 2.38, 3.80, 3.95 (each 3H, s), 5.20 (2H, s), 6.86 (1H, dd, J=8.0, 2.0 Hz), 6.91 (1H, d, J=2.0 Hz), 7.22 (1H, d, J=8.0 Hz), 7.38, 7.48, and 8.33 (each 1H, s)].

Dehydrogenation of 4c by Dichlorodicyanobenzoquinone α-Conidendrin diacetate (**4c**) (150 mg), prepared from α-conidendrin (**4d**), and dichlorodicyanobenzoquinone (210 mg) were refluxed in benzene for 3 days. The reaction mixture was extracted with 5% NaOH aqueous solution then the organic layer was purified on silica gel to yield **3b** (51 mg).

Methylation of 3a with Diazomethane Excess diazomethane in ether was poured into a solution of **3a** (30 mg) in 3 ml of methanol and the mixture was left to stand for 1 d. After purification, it gave dimethyl-detetrahydroconidendrin (**3c**)[13] (10 mg).

Acetylation of Formosanol (4a) Compound **4a** (50 mg) was treated with Ac_2O and pyridine as usual to yield the diacetate (**4e**) (50 mg) [mp 98—99 °C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1605, 1210, 1125, 1085, 1050, 935, 750. ^{1}H-NMR ($CDCl_3$) δ: 2.20, 2.24, 3.36, 3.74, and 3.81 (each 3H, s), 2.26—3.16 (4H, m, H-2, H-3, H-4), 3.41—3.96 (3H, m, H-1, H-2a), 4.99 (1H, d, J=4.4 Hz), 6.45, 6.65, and 6.75 (each 1H, s), 6.69 and 6.96 (each 1H, d, J=7.9 Hz)].

Methylation of Formosanol (4a) Formosanol (**4a**) (21 mg), dimethyl sulfate (100 mg) and potassium carbonate (210 mg) were added to anhydrous acetone (10 ml), and the mixture was heated under reflux for 5 h. After evaporation of the acetone, the residue was dissolved in $CHCl_3$ (30 mg) and then 2 N H_2SO_4 aqueous solution was added slowly. The aqueous layer was extracted with $CHCl_3$ three times and the extract was purified on silica gel to yield the pentamethoxy derivative (**4f**) (18 mg) [mp 67—68 °C. IR ν_{max}^{KBr} cm^{-1}: 1605, 1595, 1505, 1250, 1210, 1090, 1020, 980, 905, 740. ^{1}H-NMR ($CDCl_3$) δ: 2.20—3.10 (4H, m), 3.38 3.58, 3.79, 3.86, and 3.88 (each 3H, s), 3.4—3.9 (3H, m), 5.00 (1H, d, J=4.1 Hz), 6.27, 6.58, and 6.75 (each 1H, s), 6.61 and 6.78 (each 1H, d, J=7.2 Hz).

Conversion of 4e to α-Conidendrin Diacetate (4d) A solution of formosanol diacetate (**4e**) (43 mg) in dry $CHCl_3$ (18 ml) was treated with freshly distilled BF_3-etherate (6 drops) and *m*-chloroperbenzoic acid (30 mg). The reaction mixture was stirred at 20 °C under N_2 for 3 h and then washed successively with diluted aqueous sodium bisulfite, aqueous sodium carbonate and water. The product was purified on silica gel to yield α-conidendrin diacetate (**4c**) (10 mg) (mp 221—223 °C).[7]

Acetylation of Junipediol (5a) Junipediol (**5a**) (21 mg) was treated with Ac_2O and pyridine as usual to yield junipediol diacetate (**5b**) (20 mg) [mp 94—95 °C. IR ν_{max}^{KBr} cm^{-1}: 1725, 1255, 1065, 995, 975, 905, 885, 750. ^{1}H-NMR ($CDCl_3$) δ: 0.2—0.6 (3H, m), 0.99, 1.01, 1.10, 1.16, 1.95 and 1.98 (each 3H, s), 4.36 (1H, dd, J=10.6, 6.6 Hz), 4.71 (1H, dd, J=10.6, 7.1 Hz)].

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