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CHINENSIOL, A NEW DIMERIC HIMACHALANE-TYPE SESQUITERPENE FROM THE ROOT OF *JUNIPERUS CHINENSIS* LINN.

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A new dimeric sesquiterpene, chinensiol, was isolated from the roots of *Juniperus chinensis* Linn. Its structure was deduced to be a dimeric *cis* -himachalane-type sesquiterpene by spectroscopic analysis and chemical evidence. The structure of the oxidative product (eleven-member ring) obtained from chinensiol was elucidated by X-ray analysis.

KEYWORDS chinensiol; *Juniperus chinensis*; Cupressaceace; dimeric *cis* -himachalene sesquiterpene; pyridinium chlorochromate

Ten species of *Juniperus* are indigenous to Taiwan. Among them, *J. squamata* and *J. formosana* grow at an altitude of 2000-3000m above sea level. We have conducted chemical studies of these two plants.[1, 2)] *J. chinesis* Linn. and *J. chinensis* L. var. kaizuca Hort ex Exdl are common ornamental trees. Chemical studies of *J. chinensis* L. var. kaizuca Hort ex Exdl have been previously reported,[3)] and these contain bisflavones, sesquiterpenes, diterpenes and lignans. As to chemical constitutents of *J. chinensis* L., there are three previous reports of isolations of biflavones and terpenes from leaves, heartwood and roots.[4)] For the present study, we reinvestigated in detailed the acetone extract of the roots of *J. chinensis* L., and a new dimeric himachalane-type sesquiterpene, chinensiol (**1a**), was isolated. This is the first isolation of a himachalane-type sesquiterpene from *Juniperus* species.

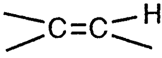
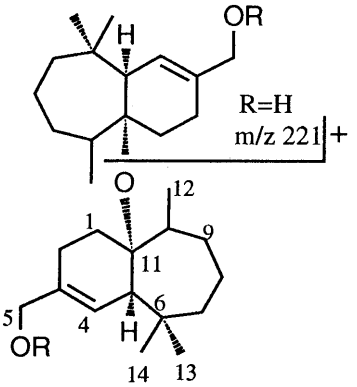
Chinensiol (**1a**), $[\alpha]_D + 40.0^o$ (C=1.0, $CHCl_3$), mp 122-123^o C, has the molecular formula $C_{30}H_{50}O_3$ on the basis of elementary analysis. The mass spectrum (EI-MS) shows fragmentation peaks at 220 (16%) and 202 (20%). But the FAB-MS (positive) exhibits a quasi-molecular ion peak at 459 [$(M + 1)^+$, 2%] and fragment peaks at 333 (12%), 285 (35%), 221 (100%), 203 (221-H_2O, 80%). The structures of fragment ions at 220 and 202 were proposed to be structures **2** and **3**, respectively. The infrared (IR) spectrum expresses absorptions at 3322 (— OH), 3010 (=C—H), 1650 and 829 (), and 1040 cm^{-1} (C— O); and the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table I) exhibits signals at 0.90 and 1.15 (each 3H, s), 1.01 (3H, d, J=6.9 Hz), 4.06 (2H, br s, $-CH_2OH$), and 5.72 (1H, br d, J=2.2 Hz, H-4). Due to the fact that only three methyl groups and one hydroxymethyl group together with about 24 protons are estimated from the ^{1}H-NMR spectrum, chinensiol (**1a**) was considered a dimeric sesquiterpenoid, not a triterpenoid. The acetylation of chinensiol (**1a**) with acetic anhydride in pyridine at room temperature gave the acetate (**1b**) (amorphous; ν_{max} 1735, 1231, and 1026 cm^{-1}; no hydroxyl group absorption band was observed). The ^{1}H-NMR spectrum of acetate (**1b**) shows one

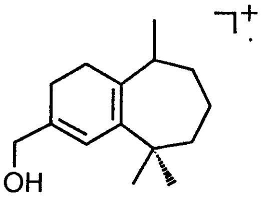
Table I. ^{1}H- and ^{13}C-NMR (δ-Values) Data for Chinensiol (**1a**) and HMBC Correlation

C		H		Carbons Correlated
1	26.6t	1-Ha	1.83	C_2, C_3, C_{11}
2	23.3t	1-Hb	1.66	C_2, C_3, C_5, C_{10}, C_{11}
3	137.3s	2-H	2.14	C_1, C_3, C_4, C_{11}
4	124.9d	4-H	5.76	C_2, C_{11}, C_{15}
5	58.8d	5-H	2.01	
6	37.1s	7-Ha	1.53	C_8
7	38.6t	7-Hb	1.50	C_5, C_6, C_{13}
8	24.2t	8-H	1.60	C_6, C_7, C_{10}
9	29.8t	9-Ha	1.48	C_8
10	41.3d	9-Hb	1.38	C_7, C_{10}
11	76.3s	10-H	2.07	C_{11}, C_{12}
12	17.8q	12-H	1.03	C_{10}, C_{11}, C_{12}
13	31.4q	13-H	0.91	C_5, C_6, C_7, C_{14}
14	26.6q	14-H	1.15	C_5, C_6, C_7, C_{13}
15	67.1t	15-H	4.07	C_2, C_3, C_4



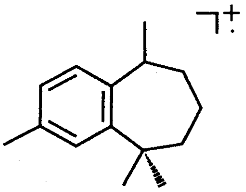
1a R=H

1b R=Ac



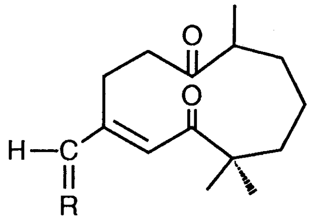
2

m/z 220



3

m/z 202



4 R=O

5 R=H, OH

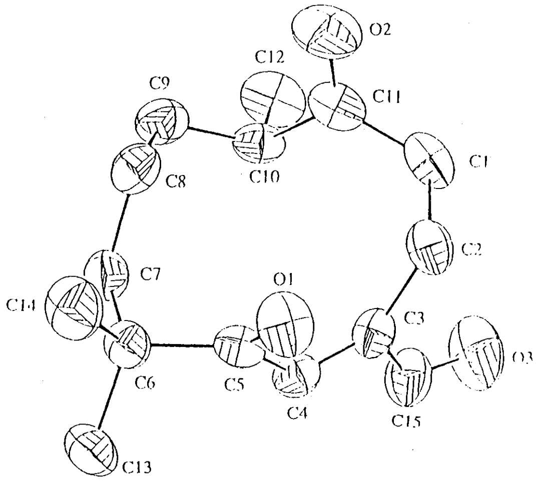


Fig. 1, Molecular Structure of 4

acetoxylmethylene absorption signal [δ 2.05 (3H, s) and 4.52 (2H, br s)]. From the above evidence, we took two oxygen atoms into account as two primary alcohols; the remaining oxygen atom was considered an ether linkage. The conclusion was confirmed by the ^{13}C-NMR (Table I)spectrum of chinensiol (**1a**). The absorption signals at δ 67.1 (2° C: by DEPT method) and 76.3 (4° C) concern two carbons bearing one oxygen atom each. By the DEPT method, the chinensiol (**1a**) is shown to contain three primary carbons, six secondary carbons, three tertiary carbons, and three quaternary carbons. Twenty-five hydrogen atoms (including one hydrogen atom from the hydroxyl group) on chinensiol (**1a**) were estimated from the above carbon state. The result confirmed that chinensiol (**1a**) is a dimeric sesquiterpene with ether linkage. The structure of chinensiol was deduced as shown in formula (**1a**) by the explanation of the ^1H-^{13}C COSY spectrum of chinensiol and the technique of HMBC (Table I) correlation. Formula (**1a**) is a dimeric himachalene-type sesquiterpene.Irradiation of 12-H (at δ 1.03) caused nuclear Overhauser enhancements on 2-Hb(19%); this experiment indicates two results. One is that himachalene-type sesquiterpene is a *cis* -fusion ring. The second is that the secondary methyl group (12-H) was considered to be on the β-face (trans to ether linkage). The dimeric himachalene-type sesquiterpene was observed for the first time, and this type of himachalane sesquiterpene was isolated for the first time in *Juniperus* species.

We tried to oxidize the chinensiol (**1a**) with pyridinium chlorochromate (PCC) in dichloromethane, and yielded an unexpected product **4**. [mp 84-85^0 C; ν_{max} 1690; λ^{MeOH}_{max} nm: 206, 230, 280; δ 0.97 (3H, d, J=7.8Hz), 1.10 and 1.21 (each 3H, s), 7.20 (1H, br s), and 9.50 (1H, s)]. The structure of the eleven-member ring product **4** was confirmed by an X-ray diffraction. Compound **4** was crystallized in orthorhombic space group P_{212121} with cell dimensions a=9.6806(17), b=10.706(7), c=13.705(5) Å, V=1420.1(11) Å^3, Z=4, F(000)=556 Dx=1.17gcm^{-3}, μ=0.6cm^{-1}, $2\theta_{max}$=49.8, total measurement 1450 reflections, crystal size 0.20 0.40 0.40mm. The crystal structure was solved by direct methods and was refined with the full matrix least squares method. H-positions were calculated according to ideal geometry. The final agreement indices are R=3.6%, RW=2.7%, S=2.39 based on 1129 observed reflections ($I>2.0\sigma(I)$). The molecular structure is shown in Fig.1. The formation pathway of product **4** is that the first intermediate **2** obtained from **1a** via acidic elimination was subsequently oxidized with PCC to yield product **5**. The dione alcohol **5** was followed by oxidizing with PCC to obtain **4**. If the primary alcohol was first oxidized with PCC, the double bond would not be converted to dione. The oxidation of enol ether with PCC was reported by Piancatelli,5) but the oxidation of tetraalkyl-substituted olefin with PCC has not been observed.

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