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A New Labdane Diterpenoid from the Bark of *Larix olgensis* Henry var. koreana Nakai

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Abstract: A new diterpenoid was isolated from the bark of *Larix olgensis* Henry var. koreana Nakai. Its structure was elucidated as 5S, 9S, 10R-labda-8 (17), 13-diene-6α, 15-diol **1** by spectroscopic methods.

Keywords: *Larix olgensis* Henry var. koreana Nakai, diterpenoid, 5S, 9S, 10R- labda-8 (17), 13-diene-6α, 15-diol.

Larix olgensis Henry var.koreana Nakai is distributed in Jilin and Heilongjiang provinces of China. Some diterpenoids have been isolated from *Larix* species[1-4], but *Larix olgensis* Henry var.koreana Nakai has not been reported. We report here a new diterpenoid from this plant.

From the EtOH extract of the bark of this plant, the $CHCl_3$ soluble partion was chromatographied on silica gel to afford compound **1** as crystal needles, mp 154℃, $[\alpha]_D^{20}$ +32.57 (c 1.0, MeOH). The ESI-MS spectrum of **1** indicated the molecular weight of 306. Its IR spectrum showed the presence of hydroxyl group (3420, 3256 cm^{-1}) and double bond (1646 cm^{-1}). The ^{1}H-NMR spectrum exhibited proton signals for one oxygenated methine (δ 3.91, 1H), one oxygenated methylene (δ 4.25, 2H) and three signals for olefilinc protons. Its ^{13}C-NMR (See **Table 1**) spectrum showed twenty carbons signals including four methyl, four methine, eight methylene and four quaternary carbons on the basis of DEPT experiment. All of the above data implied that **1** is a labdane diterpenoid by comparing with those of larixol[5], isolated from this plant. That the hydroxymethyl group linkage of C-14 (double bond carbon) was determined by the HMBC correlations from H-15 (δ 4.25, 2H) to C-14, C-13, C-16 and C-12. The HMBC spectrum also showed the corrections from H-7 to C-4, C-5, C-6, C-8, C-9 and C-17, suggesting the other double bond between C-8 and C-17. Therefore the structure of **1** was elucidated as 5S, 9S, 10R-labda-8 (17), 13-diene-6α, 15-diol. The stereostructure of **1** was elucidated by X-ray crystallographic analysis (see **Figure 1**).

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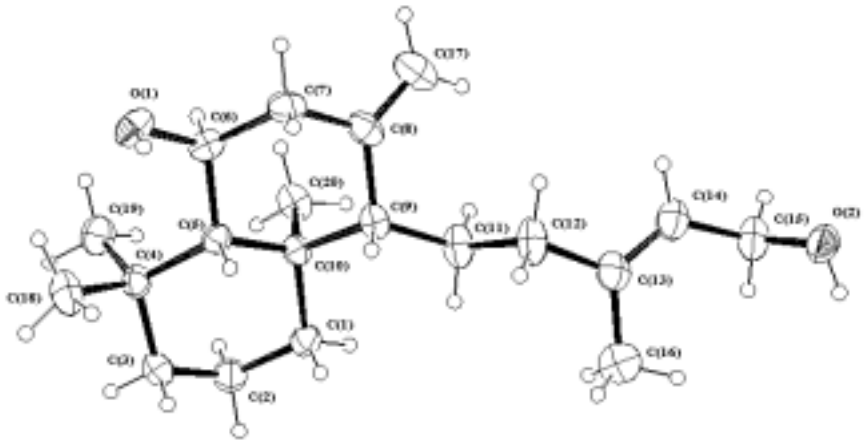
Figure 1 XRD of 1



Crystal size = 0.45*0.40*0.30 mm^3. Unit cell dimensions: a = 7.2531(15) A, b = 12.642(3) A, c = 20.299(4) A. Volume = 1861.3(7) A^3. Z = 4. Calculated density = 1.094 mg/m^3.

Table 1 ^1H, ^{13}C-NMR data of **1**

No.	δ_C	δ_H (J_{HZ})	No.	δ_C	δ_H (J_{HZ})
1	40.87	1.91 (m) 1.25 (m)	11	23.46	1.85 (m) 1.61 (m)
2	20.55	1.65 (m) 1.75 (m)	12	39.83	2.05 (m) 2.35 (m)
3	45.40	1.45 (m) 1.55 (m)	13	140.26	
4	35.22		14	125.18	5.50 (m)
5	61.61	1.32 (d, 12.9)	15	59.71	4.25 (d, 6.7)
6	72.45	3.91 (m)	16	16.58	0.85 (s)
7	50.18	2.25 (dd, 11.7, 11.5) 2.80 (dd, 4.8, 12.2)	17	108.55	4.78 (d, 1.1) 5.08 (d, 1.1)
8	147.78		18	23.07	1.18 (s)
9	56.97	1.85 (m)	19	37.49	1.35 (s)
10	40.59		20	16.94	1.85 (s)

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