

A New Bislabdane-type Diterpenoid from *Cunninghamia lanceolata*

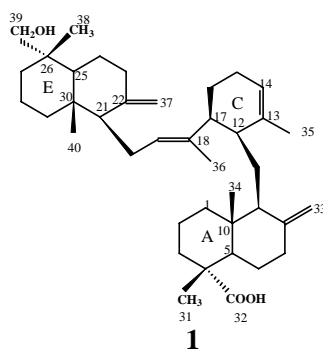
Jiang DU, Ming Lei WANG, Ruo Yun CHEN and De Quan YU*

Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050

Abstract: A new bislabdane-type diterpenoid lanceolactin (**1**), was isolated from the roots of *Cunninghamia lanceolata*. Its structure was elucidated on the basis of spectroscopic methods, especially 2D-NMR techniques.

Keywords: *Cunninghamia lanceolata*, bislabdane-type diterpenoid; lanceolactin.

Cunninghamia lanceolata Hook. is a traditional Chinese medicine used for the treatment of hernia, arthritis and strangury. Its chemical constituents have been examined^{1, 2, 3, 4}. In a previous paper we reported a bislabdane-type diterpenoid lanceolactic acid from the roots of the plant⁵. Further chemical studies on this plant led to the isolation of another new bislabdane-type diterpenoid, named lanceolactin (**1**).



Compound **1** was obtained as white amorphous powder. mp 232–234 °C, $[\alpha]_D^{18}$ -24 (c 0.10, CHCl₃). The negative HRFABMS exhibited a [M-H]⁻ peak at *m/z* 589.4653 corresponding to the molecular formula C₄₀H₆₂O₃ ([M-H]⁻ calcd. 589.4621). The presence of carboxyl groups (1701cm⁻¹) and double bonds (1645, 895cm⁻¹) was indicated by the IR spectrum. The ¹H NMR experiment suggested that compound **1** contains six methyl groups, one hydroxymethyl, six olefinic protons. Comparison of the spectral data of **1** with those of lanceolactic acid showed that both of them were constructed by a Diels-Alder cycloaddition of two diterpene monomer

units. However, lanceolatic acid was constructed by two identical monomers (12E-8 (17)-12, 14-labdatrien-18-oic acid) while **1** was by different monomers (12E-8 (17), 12, 14-labdatrien-18-ol and 12E-8 (17)-12, 14-labdatrien-18-oic acid). There are two ways in which the Diels-Alder cycloaddition reaction could occur, either head-to-head or head-to-tail. Furthermore, one monomer should serve as diene and the other as dienophile in the Diels-Alder cycloaddition reaction. Then, there are four possibilities for the structure. As seen from the ^{13}C - ^1H COSY spectrum, the chemical shift difference of two protons connected with δ_{C} 107.8 (δ_{H} 5.00 - 4.73) were more than that of two protons attached to δ_{C} 107.6 (δ_{H} 4.96 - 4.86). It is because that one proton was shielded and the other was deshielded by the double bond between C-18 and C-19. Therefore, the monomer contained δ_{C} 107.8 should be as dienophile in the Diels-Alder cycloaddition. The carbon at C-21 (δ 58.0) showed correlations with H-37 (δ 4.73, 5.00) and H-40 (δ 0.94); C-25 (δ 48.5) correlated with H-40 (δ 0.94) and H-38 (δ 0.83), as well as C-39 (δ 71.4) correlated with H-38 (δ 0.83) in its HMBC spectrum. All these correlations indicated that the monomer including hydroxymethyl supported dienophile and the other monomer contained carboxyl as diene in Diels-Alder cycloaddition. The chemical shifts (C-12 to C-17) in the ^{13}C -NMR spectrum of **1** showed similarities to those of lanceolatic acid. The HMBC spectrum of **1** showed cross peak between the signals at δ_{C} 137.5 (C-18) and δ_{H} 2.17 (H-12). It confirmed that the linkage pattern of compound **1** is the same as lanceolatic acid should be head-to-head in Diels-Alder cycloaddition. A NOESY experiment on **1** showed that the two quaternary methyl groups in rings A and E have a *cis* relationship. The relative configuration of C-9, C-12 and C-17 was also established by NOESY experiment. But the correlation of H-36 and H-19 was not observed in the NOESY spectrum, which indicated the double bond between C-18 and C-19 should be *trans* arrangement.

Table 1. ^{13}C -NMR (125MHz) data of compound **1** ($\text{C}_5\text{D}_5\text{N}$, δ , ppm, TMS)

NO.		NO.		NO.		NO.	
1	37.7 (t)	11	23.7 (t)	21	58.0 (d)	31	17.4 (q)
2	19.2 (t)	12	38.8 (d)	22	149.4 (s)	32	180.9 (s)
3	38.4 (t)	13	139.5 (s)	23	38.6 (t)	33	107.6 (t)
4	47.8 (s)	14	121.8 (d)	24	26.3 (t)	34	14.5 (q)
5	50.9 (d)	15	26.3 (t)	25	48.5 (d)	35	23.6 (q)
6	27.7 (t)	16	24.5 (t)	26	47.8 (s)	36	19.4 (q)
7	38.8 (t)	17	46.3 (d)	27	39.5 (t)	37	107.8 (t)
8	149.4 (s)	18	137.5 (s)	28	21.9 (t)	38	18.2 (q)
9	54.0 (d)	19	125.5 (d)	29	36.2 (t)	39	71.4 (t)
10	40.2 (s)	20	23.6 (t)	30	39.8 (s)	40	14.6 (q)

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