第 17 卷 第 4 期 化 学 物 理 学 报 Vol. 17, No. 4
2004 年 8 月 CHINESE JOURNAL OF CHEMICAL PHYSICS Aug. 2004

1003-7713/2004/04-454-5

(6aR,11aR)-3-羟基-4,9-二甲氧基紫檀烷分子的晶体结构

邓雁如[a], 江艳烽[b], 席婵娟[b], 武水仙[a], 汪汉卿[a*]

(a. 中国科学院兰州化学物理研究所, OSSO 国家重点实验室, 兰州 730000;
b. 清华大学化学系, 北京 100084)

摘 要: 从多刺锦鸡儿(豆科)中分离得到一个紫檀烷型化合物—(6aR,11aR)-3-羟基-4,9-二甲氧基紫檀烷,通过红外光谱、质谱、核磁共振氢谱、核磁共振碳谱、氢核-氢核相关谱、异核多量子相干谱和异核多键相干谱进行结构鉴定. 其单晶经 X 射线衍射测试表明,该化合物晶体属单斜晶系,空间群为 $P2_1$,化学式为 $C_{17}H_{16}O_5$, Mr = 300.30. 晶胞参数为: a = 6.4778(13), b = 12.631(3), c = 8.8368(18) Å, β = 95.80(3)°, V = 719.3(3) Å^3, Z = 2, Dc = 1.386 Mg/m^3, F(000) = 316, μ = 0.102 mm^{-1}. 结构由直接法解出,用全矩阵最小二乘法修正,最终偏离因子 R = 0.0332, wR = 0.0862. 该分子由一个苯并吡喃环和苯并呋喃环组成, X 射线衍射测试表明其绝对构型为顺式紫檀烷型.

关键词: (6aR,11aR)-3-羟基-4,9-二甲氧基紫檀烷;分离;晶体结构

中图分类号: **文献标识码:** A

Crystal Structure of (6aR,11aR)-4,9-dimethoxy-3-hydroxypterocarpan

Deng Yanru[a], Jiang Yanfeng[b], Xi Chanjuan[b], Wu Shuixian[a], Wang Hanqing[a*]

(*a. State Key Laboratory of OSSO, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou* 730000;
b. Department of Chemistry, Tsinghua University, Beijing 100084)

Abstract (6aR,11aR)-4,9-dimethoxy-3-hydroxypterocarpan was isolated from the natural plant of *Caragana spinifera* Kom (Leguminosae). The structure was elucidated by infrared spectra (IR), mass spectrometry (MS), ^{1}H-Nuclear magnetic resonance (^{1}H-NMR), ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR), ^{1}H-^{1}H correlation spectroscopy (^{1}H-^{1}H COSY), heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence (HMBC). In addition, its crystal structure was determined by the single-crystal X-ray diffraction analysis. It crystalized in monoclinic, space group $P2_1$ with a = 6.4778(13), b = 12.631(3), c = 8.8368(18) Å, β = 95.8(3)°, $C_{17}H_{16}O_5$, Mr = 300.30, V = 719.3(3) Å^3, Z = 2, Dc = 1.386 Mg/m^3, F(000) = 316, μ = 0.102 mm^{-1}, the final R = 0.0332 and wR = 0.0862 for 1533 observed reflections ($I > 2\sigma(I)$). The molecular backone of the compound includes a benzofuro and a benzopyran. The X-ray analysis shows that the absolute configuration of the compound is cis-pterocarpan.

Keywords (6aR, 11aR)-4,9-dimethoxy-3-hydroxypterocarpan, Isolation, Crystal structure

* Corresponding author, E-mail: whqwt@hotmail.com Received 13 November 2003; in final form 2 March 2003.

1 Introduction

Caragana (Leguminosae) is a genus comprising 80 species, with more than 60 being distributed in China[1]. Some species of this genus have been used in China and Korea as a folk medicine for the treatment of asthenia syndrome, vascular hypertension, leukorrhagia, bruises and contused wounds[2,3]. *Caragana spinifera* Kom, a species of *Caragana*, is widespread in Tibet[1]. The phytochemical studies of *Caragana spinifera* Kom have not been reported. To find new bioactive substances, we have investigated the chemical components of *Caragana spinifera* Kom collected from Tibet of China, which led to the isolation of ten compounds. Among these compounds, (6aR, 11aR)-4,9-dimethoxy-3-hydroxypterocarpan was obtained as crystals. Although the compound has been isolated from other plants[4,5], it was isolated from *Caragana spinifera* Kom for the first time. To clarify its absolute configuration, the isolated compound was full characterized byits X-ray crystallographic studies.

2 Experimental

2.1 Instrument

Melting points were determined on a X-4 micro-melting point apparatus and were uncorrected. IR spectra were recorded on an IFR-120HR spectrometer. NMR spectra were performed on an INOVA-400 using TMS as an internal standard. NMR experiments include ^{1}H-NMR, ^{13}C NMR, ^{1}H-^{1}H COSY, HMQC and HMBC. EIMS was measured on a VG-ZAB-HS mass spectrometer.

2.2 Extraction and isolation

The whole plants of *Caragana spinifera* Kom (5.0 kg) were collected from Tibet in September 2003, and were identified by Professor Suo Yourui of the North-Western Plateau Institute of Biology, CAS. The air-dried whole plants were powdered and extracted with EtOH at room temperature for three times. The extract was concentrated under vacuum to give a dark brown syrup. The syrup was suspended in water and extracted with petroleum ether, $CHCl_3$ and EtOAc, successively. The EtOAc layer was concentrated to give a black syrup which was subjected to chromatography on silica gel, and eluted with a gradient of $CHCl_3$ and MeOH to afford compound (6aR,11aR)-4,9-dimethoxy-3-hydroxypterocarpan (90 mg).

The compound crystallized as colorless crystals ($CHCl_3$-MeOH). Mp: 168 ~ 170℃; IR (KBr disk) ν (cm^{-1}): 3427、2944、1620、1516、1498、1333、1238、1144、1077、945; EIMS *m/z*: 300(M^+,100)、285(35)、164(6)、161(15)、148(33)、77(20)、57(37)、43(43); Formula: $C_{17}H_{16}O_5$; ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.02(1H, d, J = 8.4 Hz, H-1)、6.55(1H, d, J = 8.4 Hz, H-2)、3.60(1H, m, H_a-6)、4.30(1H, dd, J = 9.2, 6.4 Hz, H_b-6)、3.58(1H, m, H-6_a)、7.24(1H, d, J = 8.0 Hz, H-7)、6.44(1H, dd, J = 8.0, 2.4 Hz, H-8)、6.41(1H, d, J = 2.4 Hz, H-10)、5.54(1H, d, J = 6.8 Hz, H-11_a)、3.68 and 3.64 (each 3H, s, 4-OCH_3, 9-OCH_3)、9.36(1H, s, OH-3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 125.6(C-1)、109.9(C-2)、135.5(C-3)、150.9(C-4)、160.5(C-4_a)、66.1(C-6)、40.8(C-6_a)、119.3(C-6_b)、125.2(C-7)、105.9(C-8)、149.5(C-9)、96.3(C-10)、160.2(C-10_a)、78.1(C-11_a)、112.5(C-11_b)、60.1(4-OCH_3)、55.2(9-OCH_3).

2.3 Crystallographic data collection and structure

A colorless platelet single crystal was mounded on a glass fiber. The determination of the unit cell and the data collection were performed with a Rigaku R-Axis Rapid IP detector equipped with a graphite monochromated MoKα radiation (λ = 7.1073 nm). At 293(2) K, a total of 1725 reflections (R_{int} = 0.0000) were collected in the range of $2.32^\circ \leqslant \theta \leqslant 27.49^\circ$, of which 1533 observed reflections with $I \geqslant 2\sigma(I)$ were used in the succeeding structure determination and refinements. The crystal structure was solved by direct methods using SHELXS-97[6] program, and refined by full matrix least-squares refinement on F^2 (SHELXL-97)[7]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. The final refinement converged at R = 0.0332 and wR = 0.0862 [$w = 1/[\sigma^2(Fo^2) + (0.0616P)^2]$, where $P = (Fo^2 + 2Fc^2)/3$], S =

1.025, $(\Delta/\sigma)_{max}=0.001$. The largest peak and deepest hole on the final difference Fourier map were 0.174 and −0.211 e/Å^3, respectively.

3 Results and discussion

The EIMS spectrum displayed a molecular ion as the base peak at $m/z=300$, corresponding to a molecular formula $C_{17}H_{16}O_5$. Its IR spectrum showed hydroxyl and C−O−C absorption bands at 3427 and 1238 cm^{-1}, respectively. The ^{1}H NMR spectrum displayed absorptions of a pterocarpan ring system at δ_H = 3.58 (1H, m), 4.30 (1H, dd, J = 9.2, 6.4 Hz), 3.60 (1H, m), 5.54 (1H, d, J = 6.5 Hz), indicating the presence of OCH_2CHCHO group. The resonances of the aromatic protons revealed the familiar ABX pattern for one of the rings (δ_H = 6.41, 6.44 and 7.24) and two doublets indicative of ortho substitution for the other (δ_H = 6.55 and 7.02, J = 8.4 Hz). Two signals at δ_H = 3.68 and 3.64 indicated the presence of two methoxyl groups. One downfield signal at 9.36 was due to a hydroxyl group. The chemical shifts in ^{13}C-NMR, ^{1}H-^{1}H COSY, HMQC and HMBC further confirmed the position of hydroxyl group and methoxyl groups. Finally, the absolute configuration of the compound can be assigned from its X-ray crystallography. The structure of the compound was elucidated as the (6aR, 11aR)-4, 9-dimethoxy-3-hydroxypterocarpan[5].

The atomic coordinates and equivalent thermal parameters for non-hydrogen atoms are listed in Table 1, and the selected bond lengths and bond angles are shown in Table 2. An ORTEP drawing of the title compound showing the molecular conformation and atom-labeling scheme is depicted in Fig. 1.

The molecular backbone of the title compound is composed of one benzofuro and one benzopyran as shown in Fig. 1. The C−C bond distances in two benzene rings ranging from 1.374(3) to 1.396(3) Å and the C−C−C angle ranging from 116.93°(18) to 123.25°(18) are normal. The furo ring defined by atoms C(12), C(11), C(5), C(6) and O(4) is shown as an envelope conformation. Two hydrogen atoms located at C(5) and C(12) respectively, shows a cis-configuration, indicating that the compound is a cis-pteranocarpans with 6aR, 11aR configuration (Fig. 1).

There exist intermolecular hydrogen bonds O(1)−H(1)···O(5) in the title compound. The bond lengths of O(2)···O(5) and H(1)···O(5) are 2.834(3) and 2.14(4), respectively, and the bond angle of O(1)−H(1)···O(5) is 139(3). The important structural feature concerning hydrogen-bonding could be found in its molecular packing (Fig. 2).

Table 1 Atomic coordinates ($\times10^4$) and equivalent displacement parameters (Å$^2\times10^3$)

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O(1)	4228(3)	4630(1)	6871(2)	52(1)	C(7)	3549(3)	11385(2)	8060(2)	38(1)
O(2)	4449(2)	5375(1)	7413(2)	43(1)	C(8)	2214(3)	12226(2)	8230(2)	38(1)
O(3)	−425(2)	7511(1)	7069(2)	40(1)	C(9)	155(4)	12186(2)	7637(3)	43(1)
O(4)	3839(2)	9618(1)	7025(2)	40(1)	C(10)	−642(3)	11273(2)	6919(2)	40(1)
O(5)	2830(3)	13152(1)	8954(2)	50(1)	C(11)	648(3)	10419(2)	6759(2)	35(1)
C(1)	3782(3)	5679(2)	6665(2)	36(1)	C(12)	289(3)	9305(2)	6184(2)	34(1)
C(2)	5253(3)	6333(2)	6104(3)	40(1)	C(13)	−496(3)	8616(2)	7426(3)	38(1)
C(3)	4817(3)	7387(2)	5864(2)	38(1)	C(14)	1484(3)	7162(2)	6770(2)	31(1)
C(4)	2946(3)	7826(1)	6215(2)	31(1)	C(15)	1888(3)	6086(2)	6984(2)	33(1)
C(5)	2493(3)	8971(2)	5934(2)	34(1)	C(16)	−178(6)	5508(3)	8901(3)	71(1)
C(6)	2714(3)	10502(2)	7303(2)	34(1)	C(17)	4769(5)	13147(2)	9860(4)	63(1)

$$U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

Table 2　Bond Lengths(Å) and Bond Angles(°)

Bond	Distances/Å	Bond	Distances/Å	Bond	Distances/Å
O(1) – C(1)	1.364(3)	C(1) – C(15)	1.385(3)	C(6) – C(7)	1.382(3)
O(2) – C(15)	1.378(2)	C(1) – C(2)	1.389(3)	C(7) – C(8)	1.388(3)
O(2) – C(16)	1.424(3)	C(2) – C(3)	1.374(3)	C(8) – C(9)	1.384(3)
O(3) – C(14)	1.363(2)	C(3) – C(4)	1.396(3)	C(9) – C(10)	1.390(3)
O(3) – C(13)	1.433(3)	C(4) – C(14)	1.391(3)	C(10) – C(11)	1.381(3)
O(4) – C(6)	1.369(2)	C(4) – C(5)	1.491(3)	C(11) – C(12)	1.506(3)
O(4) – C(5)	1.479(2)	C(5) – C(12)	1.526(3)	C(12) – C(13)	1.528(3)
O(5) – C(8)	1.373(3)	C(6) – C(11)	1.380(3)	C(14) – C(15)	1.393(3)
O(5) – C(17)	1.415(3)				
Angle	(°)	Angle	(°)	Angle	(°)
C(15) – O(2) – C(16)	116.1(2)	O(4) – C(5) – C(12)	104.53(15)	C(6) – C(11) – C(12)	107.43(17)
C(14) – O(3) – C(13)	114.07(16)	C(4) – C(5) – C(12)	114.55(16)	C(10) – C(11) – C(12)	133.66(19)
C(6) – O(4) – C(5)	106.16(14)	O(4) – C(6) – C(11)	113.00(17)	C(11) – C(12) – C(5)	101.13(16)
C(8) – O(5) – C(7)	117.2(2)	O(6) – C(6) – C(7)	123.75(17)	C(11) – C(12) – C(13)	109.92(17)
O(1) – C(1) – C(15)	120.9(2)	C(11) – C(6) – C(7)	123.25(18)	C(5) – C(12) – C(13)	109.31(16)
O(1) – C(1) – C(2)	118.76(19)	C(6) – C(7) – C(8)	116.93(18)	O(3) – C(13) – C(12)	112.08(17)
C(15) – C(1) – C(2)	120.36(19)	O(5) – C(8) – C(9)	115.57(19)	O(3) – C(14) – C(4)	122.42(18)
C(3) – C(2) – C(1)	119.59(18)	O(5) – C(8) – C(7)	123.26(19)	O(3) – C(14) – C(15)	116.81(17)
C(2) – C(3) – C(4)	121.36(19)	C(9) – C(8) – C(7)	121.16(19)	C(4) – C(14) – C(15)	120.71(17)
C(14) – C(4) – C(3)	118.42(18)	C(8) – C(9) – C(10)	120.2(2)	O(2) – C(15) – C(1)	117.00(18)
C(14) – C(4) – C(5)	120.94(17)	C(11) – C(10) – C(9)	119.60(19)	O(2) – C(15) – C(14)	123.35(18)
C(3) – C(4) – C(5)	120.58(17)	C(6) – C(11) – C(10)	118.74(18)	C(1) – C(15) – C(14)	119.52(18)
O(4) – C(5) – C(4)	109.51(15)				

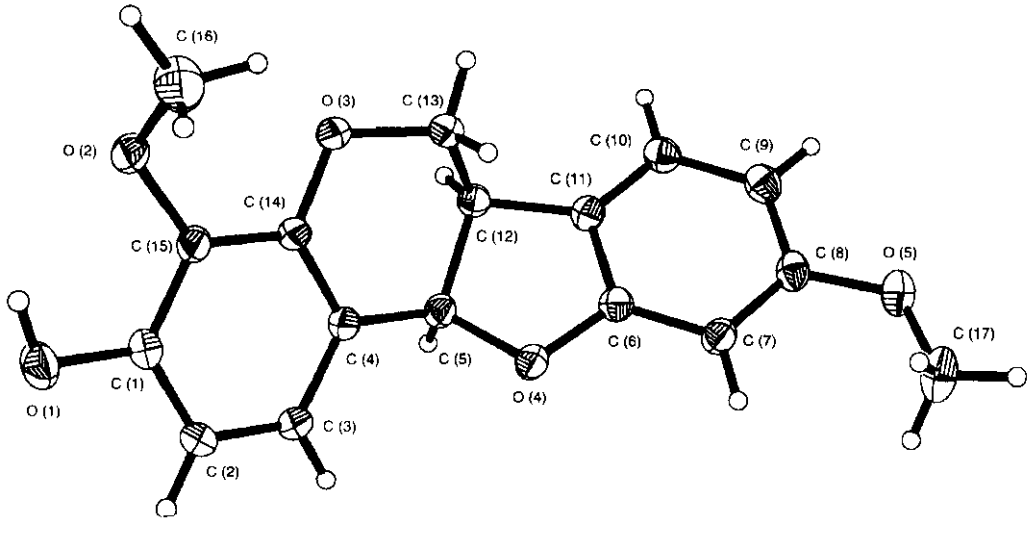

Fig. 1　Molecular structure of title compound at 30% ellipsoid probability

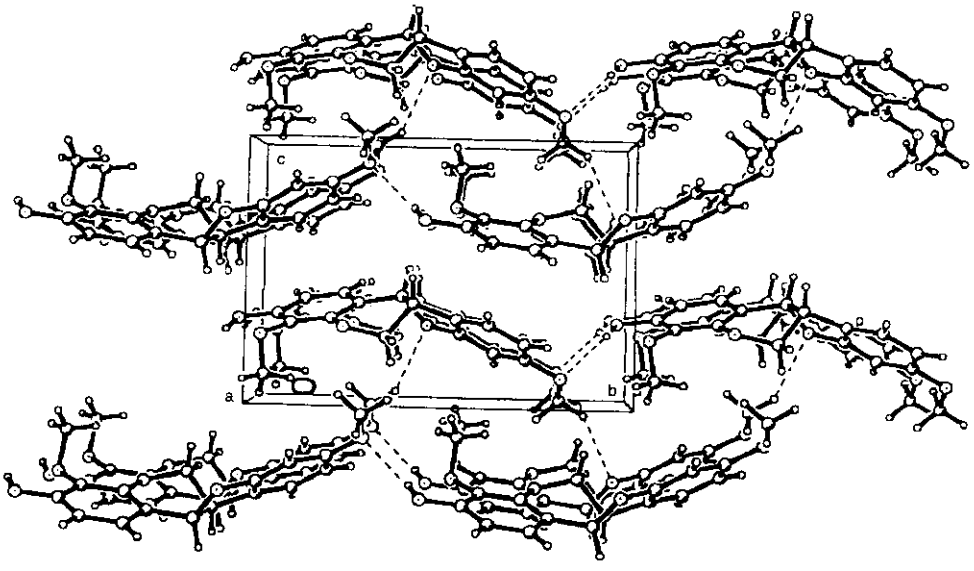

Fig. 2 Packing diagram of title compound, showing the intermolecular hydrogen-bonding network along the *b* axis

References

[1] Wu Cheng-yih. Xizangzhiwuzhi, Beijing: Science press, 1985, **2**: 779

[2] Luo Hongfeng, Zhang Liping, Hu Changqi. *Tetrahedron*, 2001, **57**: 4849

[3] Kitanaka S, Takido M, Mizoue K, Kondo H, Nakaike S. *Chem. Pharm. Bull.*, 1996, **44**: 565

[4] Spencer G F, Jones B E, Plattner R D, Barnekow D E, Brinen L S, Clardy J. *Phytochemistry*, 1991, **30**: 4147

[5] Ingham J L, Dewick P M. *Phytochemistry*, 1979, **18**: 1711

[6] Sheldrick G M. SHELXS-97. Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.

[7] Sheldrick G M. SHELXL-97. Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.