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菠萝香藤的倍半萜成分

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摘要 从菠萝香藤(*Kadsura ananosma*)中分离到 3 个新的对映桉烷型倍半萜成分,分别命名为菠萝香藤素(ananosmin)(2),菠萝香藤甙甲(ananosmoside A)(3) 和菠萝香藤甙乙(ananosmoside B)(4),通过化学及光谱学方法确定了它们的结构。同时, 还分离到已知的 β–chaenocephalol cinnamate (1),β–谷甾醇(β–sitosterol)(6)和胡萝卜甙(daucosterol)(7)。

关键词 菠萝香藤; 倍半萜; 菠萝香藤素; 菠萝香藤甙甲; 菠萝香藤甙乙

SESQUITERPENOIDS FROM KADSURA ANANOSMA

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Abstract The investigation of the stems of *Kadsura ananosma* afforded a new enantio–eudesmanolide and two new enantio– eudesmanlide– β – D–glucopyranosides, named ananosmin(2),ananosmoside A(3), ananosmoside B(4), respectively. The structures were elucidated by spectral data and chemical transformation. In addition, β–chaenocephalol cinnamate(1), β–sitosterol(6) and daucosterol(7) were also obtained.

Key words *Kadsura ananosma;* Sesquiterpene; Ananosmin; Ananosmoside A;Ananosmoside B

INTRODUCTION

The genus *Kadsura* (Schisandraceae) has been proved to be a good source of dibenzooctadiene lignans, but there have been very few reports of the isolation of sesquiterpenoids from these plants. The present paper describes the isolation and elucidation of three new sesquiterpenoids, ananosmin(2), ananosmoside A(3),ananosmoside B(4).

RESULTS AND DISCUSSION

One of the sesquiterpenoids isolated from *K.ananosma* was identified readily as β–chaenocephalol cinnamate (1), which had been found previously in *Verbesina rupestris* [1].

The ^{13}C DEPT spectrum of ananosmin (2) gave the resonances of 15 carbons (CH3,4; CH2,4; CH,5; C,2). Assignments were made listed in Table 2. A tertiary and two secondary hydroxy groups could be

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deducedfrom DEPT spectrum(74.3, C; 74.0, CH; 80.2, CH) and mass spectrum (m / z):238(M^+-H_2O),220(M^+-2H_2O), 202(M^+-3H_2O). ^{1}H NMR spectrum showed the resonances of the isopropyl group (0.95 and 1.10, each 3H, d, J = 6.5Hz), the tertiary C–15 and C–14 methyl groups (0.95 and 1.32, each 3H, s).

A ^{1}H signal(4.33, dd, J = 11.5 and 4.3Hz) and another ^{1}H signal (1.71, d, J = 11.6Hz) indicated the presence of an equatorial hydroxy group at C–6. Acetylation of ananosmin (2) gave a monoacetate (5) . The signals at 3.25(1H, dd, J = 8 and 7Hz) and 80.2(CH) in(2) were shifted downfield to 4.60 (1H,dd, J = 11.0 and 4.2Hz) and 82.3 (CH) suggesting the acetylation position was at C–1.

Analysis of the spectral data of β–chaenocephalol cinnamate (1),ananosmin (2) and the acetate (5) sugessted (2) was a 1 α , 4, 6 β–trihydroxy–enantio–eudesmane which was related structurally to β–chaenocephalol cinnamate (1) .

^{13}C NMR spectra (in $CDCl_3$) of analogous compounds showed a signal at 20—21ppm (C–14) with an axial 4–hydroxy group [2] but a signal at 23—25ppm (C–14) with an equatorial hydroxy. The acetate (5) was deduced bearing an equatorial hydroxy group at C–4 for its ^{13}C NMR (in $CDCl_3$) showed the signal of C–14 was at 23.8ppm. Thus the structure of ananosmin (2) was comfirmed as shown in (2).

The DEPT and ^{1}H NMR spectra of ananosmoside A (3) showed extreme resemblance with ananosmin (2) except a typical β–glucose resonances (anomeric H:δ4.53, d, J = 7.7Hz). Hydrolysis of ananosmoside A (3) with subsequent PC against an authentic sample in two different developers established that the sugar was a glucose. The aglycone moiety was determined identical with ananosmin(2) by comparisons of spectral data of ^{1}H NMR and ^{13}C NMR, TLC and mixed melting point.

Compared with ananosmin (2), the downfield shift of C–6 and C– 6 proton in ^{13}C NMR and ^{1}H NMR spectra of ananosmoside A (3) indicated the β–glucopyranosyl group at C–6. The unusual upfield shift of C–7 in ^{13}C NMR could be accounted for as the sugar made the steric hinderance at C–7 considerably larger.

The DEPT and ^{1}H NMR spectra of ananosmoside B (4) showed analogous resonances with ananosmoside A (3) except typical signals of a benzoxy group. Saponification of ananosmoside B(4) with subsequent TLC against ananosmoside A (3) in two different developers showed that the alcohol moiety was identical with ananosmoside A (3).

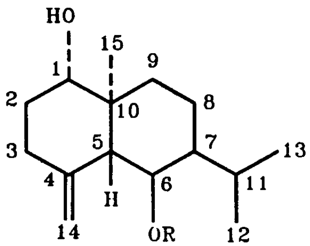
The downfield shift of C–1 in the ^{13}C NMR spectrum of ananosmoside B (4), when compared with ananosmoside A (3), indicated the benzoxy group at C–1.

β–sitosterol(6) and daucosterol(7) were also isolated and determined by comparing with authentic samples.

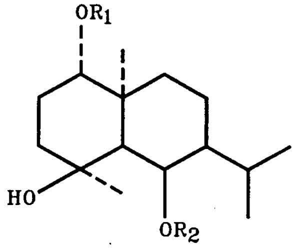
EXPERIMENTAL SECTION

MS (20eV) direct insertion. $[\alpha]_D^{20}$: CH_3OH. UV: EtOH. IR: KBr. Chromatographic separations were carried out on silica gel. TLC was performed on silica gel G using $CHCl_3$–MeOH as developer. Spots were detected heating to 100℃ in an oven after spraying with H_2SO_4(10%).

Extraction and isolation Stems of *K. ananosma* were collected during September from Mengla, Yunnan, China, and identified by Prof. Guo–Da Tao, Xishuangbanna Tropical Botanical Garden, Academia Sinica. The air–dried plant material (10kg) were extracted with EtOH . The extracts were evaporated to dryness in vacuo to give a residue (250g) which was directly applied to silica gel column. Sequential elution with $CHCl_3$ and $CHCl_3$–MeOH with increasing MeOH content, gave fractions which were combined according to their Rf value on TLC. Every fraction was repeatedly chromatographed until pure compounds were obtained. Reverse phase CC was used when glycosides were isolated. Fraction eluted with $CHCl_3$gave 40mg (1) while fraction eluted with $CHCl_3$–MeOH (9:1) gave 50mg (2). 70mg ananosmoside A (3) and 45mg ananosmoside B(4) were obtained and purified by reverse phase CC.



1) R=Cinnamoyl



2) R1=R2=H 4) R1=Benzoyl, R2=glc
3) R1=H, R2=glc 5) R1=Acetyl, R2=H

Table 1 ^{1}H NMR Chemical shifts and coupling constants*

H	2	3	4	5
1	3.25(1H,dd,J=8.7)	1.94(1H,d,J=11.6)	4.81(1H,dd,J=11.6,4.6)	4.60(1H,dd,J=11.0,4.2)
5	1.71(1H,d,J=11.6)	4.67(1H,dd,J=11.4,4.4)	2.13(1H,d,J=11.8)	1.83(1H,d,J=11.4)
6	4.33(1H,dd,J=11.5,4.3)	2.21(1H,m,J=6.7)	4.73(1H,dd,J=11.8,1.5)	4.34(1H,dd,J=11.4,4.7)
11	2.05(1H,m,J=6.5)	0.99(3H,d,J=6.7)	2.24(1H,m,J=5.8)	
12	0.95(3H,d,J=6.5)	1.10(3H,d,J=6.7)	0.99(3H,d,J=5.8)	0.92(3H,d,J=6.7)
13	1.10(3H,d,J=6.5)	1.40(3H,s)	1.12(3H,d,J=5.8)	1.11(3H,d,J=6.7)
14	1.32(3H,s)	0.97(3H,s)	1.48(3H,s)	1.37(3H,s)
15	0.95(3H,s)	4.53(1H,d,J=7.7)	1.25(3H,s)	1.03(3H,s)
anomeric			4.55(1H,d,J=6.8)	
benzoxy moiety			7.98(2H,d,J=7.3, 2′,6′–H)	
			7.47(2H,t,J=7.3, 3′,5′–H)	
			7.60(1H,t,J=7.3, 4′–H)	

* Recorded in CD_3OD except 5 (in $CDCl_3$

β–chaenocephalol cinnamate(1) IRν_{max}^{KBr}cm^{-1}: 3400, 1700, 1670, 1570, 1440, 973, 900, 875, 840; UVλ_{max}^{EtOH}nm: 207.0, 213.0, 250. 0(24800,15100, 22000); ^{1}H NMR (in $CDCl_3$): 6.40(1H, d, J=16Hz, φ–CH=CH–CO–), 7.65(1H ,d, J=16Hz, φ–CH=CH–CO–), 7.40(5H, m, C_6H_5–CH=CH–CO–), 5.36(1H, dd, J=11.9, 5.0Hz, H–6), 4.85 and 4.35(each 1H, s, =CH_2), 3.51(1H, dd, J=11. 5, 4.8Hz, H–1), 0.99 and 0.95 (each 3H, d, J=6.5Hz, C–12 and C–13 methyls), 0.85(3H, s, C–15 methyl); ^{13}C NMR: see Table 2.

Ananosmin (2) colourless needles, mp 174—175℃. IRν_{max}^{KBr}cm^{-1}: 3260,2930, 1385, 1360; MS m/z: 238, 220, 202, 195, 177, 43; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2.

Ananosmin acetate (5) A soln of ananosmin (2) (20mg) in Py (1.0ml) and Ac_2O (1.0ml) was left to stand overnight at room temperature. Removal of the solvent gave the gummy acetate (5) quantitatively; ^{1}H NMR: See Table 1; ^{13}C NMR: see Table 2.

Ananosmoside A (3) pale yellow gum. IR$\nu_{max}^{KBr}cm^{-1}$: 3395, 2930, 1077 , 1050; MS m/z: 236, 218, 203, 192, 185, 175; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2. $[\alpha]_D^{20}$: −18.6.

Table 2 ^{13}C NMR chemical shifts

Carbon	No.	1^b	2^a	3^a	4^a	5^a	5^b
aglycone	1	79.2	80.2	80.3	83.0	82.3	80.4
moiety	2	31.6	28.7	28.7	25.7	25.8	25.4
	3	35.2	40.8	40.7	40.4	40.5	40.0
	4	144.0	74.3	74.1	73.7	73.7	72.6
	5	47.2	50.9	51.4	51.5	51.2	50.5
	6	73.1	74.0	79.6	79.0	73.7	73.4
	7	42.8	48.3	42.5	42.4	c	47.4
	8	22.4	23.6	23.6	23.4	23.7	22.3
	9	32.2	36.9	36.7	36.9	36.7	35.6
	10	42.4	41.9	42.8	42.2	41.1	40.0
	11	25.4	26.3	26.4	26.4	26.5	24.9
	12	22.2	22.7	23.0	23.0	22.9	22.3
	13	24.0	24.9	24.1	24.1	25.0	24.4
	14	108.3	23.8	23.8	23.7	24.0	23.8
	15	12.0	14.5	14.4	15.6	15.4	15.0
sugar	1			100.2	100.2		
moiety	2			75.8	75.9		
	3			78.4	78.4		
	4			72.0	72.1		
	5			78.1	78.3		
	6			63.2	63.2		
cinnamoyl		166.7					
moiety		118.6					
		144.9					
		134.6					
		128.8					
		128.1					
		130.2					
benzoxy	C=O				167.7		
moiety	1				131.7		
	2,6				130.4		
	3,5				129.6		
	4				134.3		
acetyl	CH_3					21.2	21.1
moiety	C=O					d	170.7

a) in CD^3OD solution. b) in $CDCl^3$solution. c) Signal obscured by the solvent signal. d) not recorded.

Hydrolysis of ananosmoside A (3). A soln of ananosmoside A (3) in 1mol/L HCl was heated in a boiling water bath for 4h. Colourless needles which were identical with ananosmin (2) (mp, ^{1}H NMR,

^{13}C NMR and TLC) were obtained. The aqueous layer was compared with authentic glucose by PC in the following solvent systems: (a) *n*–BuOH–AcOH–H^2O (4:1:5, v / v / v); (b) *n*–BuOH–EtOH–H_2O (4:1:2.2, v / v / v). In the two cases the Rf value of the unknown sugar was identical with that of glucose.

Ananosmoside B (4) colourless gum, IR$\nu_{max}^{KBr}cm^{-1}$: 3420, 3060, 2920,1713, 1600, 1510, 1450, 1070, 1044, 715; MS m / z: 342, 325, 299, 220, 203, 163, 105, 73, 43; ^{1}H NMR: see Table 1; ^{13}C NMR : see Table 2.

Saponification of ananosmoside B (4). ananosmoside B (4) was treated with 2% potassium hydroxide at room temperature for a night. The mixture was acidified with hydrochloric acid and evaporated in vacuo. The residue was extracted with MeOH. The MeOH extracts were compared with ananosmoside A (3) by TLC in the following systems: (a) $CHCl_3$–MeOH(9:1, v / v), (b) CH_3OH–H_2O (8:2, v / v, on a Rp–8 plate) . In the two cases the Rf value of the alcohol moiety was identical with that of ananosmoside A (3).

***β*–Sitosterol(6)** colorless needles, mp 140℃ . IR$\nu_{max}^{KBr}cm^{-1}$: 3500, 2930, 1470, 1380, 1065, 960; MS: m / z: 414, 396, 381, 329, 303, 273,255, 213, 43. Melting point, IR, TLC were identical with an arthentic sample.

Daucosterol(7) amorphous powder. mp >300℃ . IR$\nu_{max}^{KBr}cm^{-1}$: 3400, 2960, 2930, 2850, 1450, 1375, 1360, 1160, 1100, 1075, 1025. IR and TLC were identical with an authentic sample.

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REFERENCES

[1] Box V G S, Bardoville V, Chan W R. Enantio–Eudesmane Sesquiterpenes from Verbesina rupestris. *Phytochemistry* 1977, **16**(7):987

[2] Brennan M R, Erickson K L. Austradiol acetate and austradiol diacetate, 4,6–dihydroxy–(+)–selinane derivative from an Australian caurencia sp. *J Org Chem* 1982; **47**(20):3917