Journal of Chemistry, Vol. 45 (1), P. 102 - 105, 2007

CHEMICAL EXAMINATION OF *POLYSCIAS SERRATA* BALF. FAMILY ARALIACEAE

Received 30 May 2006

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SUMMARY

*A mixture 3-O-β-D-glucopyranosylstigmasta-5,22-diene **1a** and 3-O-β-D-glucopyranosylstigmasta-7,22-diene **1b**, 1'-O-benzyl-β-D-glucopyranoside **2** and (8Z)-2-(2-hydroxypentacosanoylamino)octadeca-8-ene-1,3,4-triol **3** were the first time isolated from Polyscias serrata. Among them, compound **3** was the first time found in the genus Polyscias.*

I - INTRODUCTION

Polyscias fruticosa (L.) Harm. has been traditionally used as tonic, anti-inflammatory [1] and some reports showed that the plant contained oleanane saponins [2]. In a program of studying phytochemistry on some plants of the genus *Polyscias* growing in Vietnam and that has not yet been studied, from *Polyscias serrata*, we isolated some compounds: a mixture of 3-*O*-β-D-glucopyranosylstigmasta-5,22-diene-3β-ol **1a** and 3-*O*-β-D-glucopyranosyl-stigmasta-7,22-diene-3β-ol **1b**, 1'-*O*-*b*enzyl-β-D-glucopyranoside **2** and (8*Z*)-2-(2-hydroxypentacosanoylamino)octadeca-8-ene-1,3,4-triol **3**.

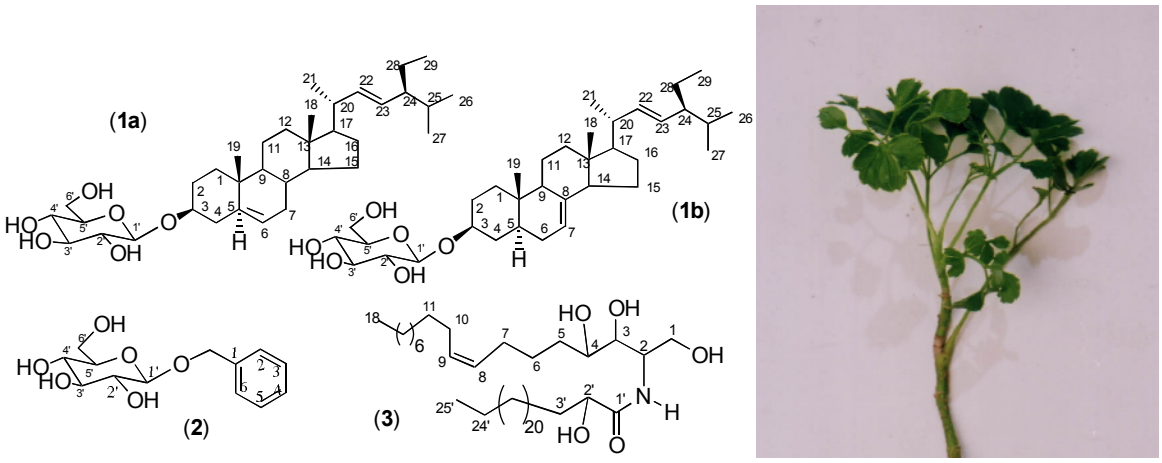

Figure 1: Polyscias serrata

II - EXPERIMETAL

1. General

IR spectra were measured in KBr, ^{1}H- and ^{13}C-NMR were recorded on Bruker Avance 500 MHz and 125 MHz, respectively in a mixture of $CDCl_3$ and CD_3OD. MS spectra were carried out on Agilent-MSD-Trap-SL.

2. Plant material

The leaves of *Polyscias serrata* were collected in Binh Duong province in June 2004. The identification of the scientific name of the plant was performed by Mrs. Lieu Ho My Trang, University of Medicine, Ho Chi Minh City.

3. Extraction and Isolation

Dried and powdered leaves (1.0 kg) of *Polyscias serrata* was exhaustively extracted with ethanol at room temperature to yield the crude extract (80 g). It was subjected successively to silica gel solid phase extraction [6] to obtain petroleum ether, chloroform and methanol fractions. The chloroform fraction was carried out on column chromatography many times with $CHCl_3$-EtOAc and EtOAc-CH_3OH to obtain **2** (6 mg). The methanol fraction (35 g) was chromatographied on silica gel column eluting with increasing amount of methanol in chloroform to yield nine fractions. Fraction 4 was carried out column chromatography with $CHCl_3$-CH_3OH (97:3) to yield **1** (75 mg) and with $CHCl_3$-CH_3OH (9:1) **3** (25 mg).

III - RESULTS AND DISCUSSION

The methanol fraction of the crude ethanolic extract of the dried and powdered leaves of *Polyscias serrata* was applied on silica gel column chromatography. After rechromatographing many times, **1**, **2** and **3** were obtained. Compound **1** was a white powder. Its IR indicated the presence of hydroxyl group at 3420 cm^{-1}. The ^{13}C-NMR spectrum of **1** contained two signals of anomeric carbon at 101.3 and 101.2 ppm. The signals at 79.3 - 62.0 ppm corresponded to glucose residue. Signals at 140.5 - 117 ppm were typical of carbon-carbon double bond of stigmasta-5,22-diene-3β-ol (C_5-C_6: 140.3 - 122.3 ppm, C_{22}-C_{23}: 138.5-129.5 ppm) and stigmasta-7,22-diene-3β-ol (C_7-C_8: 117.5 - 139.7ppm, C_{22}-C_{23}: 138.4 - 129.6 ppm). Thus, by comparing with authentic samples [3] **1** was determined as a mixture of the two above-mentioned compounds.

The compound **2** was isolated from chloroform fraction. Its ^{1}H-NMR revealed signals of a monosubstituted-benzene at 7.30 - 7.38 ppm; of a β-D-glucopyranoside at 4.40 - 3.36 ppm in which the anomeric proton appeared as a doublet with J = 7.5 Hz at 4.40 ppm. There were also two doublets at 4.91 and 4.67 ppm, each had J = 11.5 Hz: that were two non-equivalent methylene protons of -O-C**H**$_2$-phenyl. Its ^{13}C-NMR spectra showed six carbons of benzene-ring at 128.1 - 137.3 ppm; six carbons of sugar at 102.23; 76.62; 76.12; 73.79; 71.49 and 62.00 δppm of respectively to carbons C-1' (acetal carbon), C-3', C-5', C-2', C-4' and C-6'. These data were compatible to those of β-D-glucopyranoside with 104.0, 76.8, 76.8, 74.1, 70.6 and 61.8 [5]. There was also one carbon of -*O*-**C**H$_2$-phenyl at 70.37 ppm. Therefore, **2** was suggested as 1'-*O*-*b*enzyl-β-D-glucopyranoside.

The IR spectrum of **3** indicated the presence of hydroxyl group at 3414 cm^{-1} and a carbonyl group of an amide at 1662 cm^{-1}. The ^{1}H-, ^{13}C- and DEPT-NMR spectra showed that compound **3** was a polyhydroxyamide with two long straight chains, contained many hydroxyl groups and on one chain there was a carbon-carbon double bond (two signals at 130.2 and 129.3 ppm). The MS spectrum of **3** could not show the molecular ion but it had a peak at *m*/*z* = 439, corresponded to $[C_{27}H_{53}O_3N]^+$ of a *N*-alkylamide. The comparison of ^{13}C-NMR spectra between **3** and the one of gynuramide [4] as well as the computational one, presented in table 1, showed that **3** also had the moiety of (2-aminooctadec-8-ene-1,3,4-triol) as in gynuramide, except for the configuration of the carbon-carbon double bond at C_8-C_9. This was determined to be *Z* configuration with the coupling constant of J = 4.0 Hz. The structure of

3 was also supported by HSQC and HMBC spectra. Other correlations observed in the HSQC and HMBC were presented in table 1, figure 2 and appendix 1.

So, we proposed that **3** is (8*Z*)-2-(2-hydroxypentacosanoylamino)octadeca-8-ene-1,3,4-triol.

Table 1: ^{1}H-NMR, ^{13}C-NMR, HMBC spectra data of compound **3** comparing to gynuramide [4]

N	Gynuramide (Pyridine-d_5) δ_C	Compound **3** ($CDCl_3$ + CD_3OD)		
		δ_C	δ_H	HMBC
1	62.0	61.3	3.73; 3.80 (dd; J = 4.0; 11.5 Hz)	H-1/C-2; H-1/C-3
2	53.0	51.8	4.09 (m)	H-2/C-3
3	76.8	75.8	3.52 (m)	H-3/C-1; H-3/C-2; H-3/C-4
4	73.0	72.4	3.52 (m)	H-4/C-3; H-4/C-5
5	34.1	32.8	1.42 ; 1.68	
6	26.7	25.9	1.42	
7	32.9	32.7	1.96	H-7/C-6; H-7/C-8
8	130.8	130.2	5.40 (dd; J = 1.0; 4.0 Hz)	H-8/C-7; H-8/C-9
9	130.7	129.3	5.40 (dd; J = 1.0; 4.0 Hz)	H-9/C-8; H-9/C-10
10	33.3	32.7	1.95	H-10/C-9; H-10/C-11
11	29.5	29.3-29.8	1.42	H-11/C-10; H-11/C-12
13-16	29.5	29.3-29.8	1.25 - 1.37	
17	-	22.8	1.30	H-17/C-16; H-17/C-18
18	14.2	14.2	0.88	H-18/C-17
1'	175.3	175.8		
2'	72.5	72.2	4.04 (dd; J = 3.5; 8.5 Hz)	H-2'/C-1'; H-2'/C-3'
3'	35.7	34.5	1.58	H-3'/C-2'; H-3'/C-4'
4'-23'	29.5	29.3-29.8	1.25 - 1.37	
24'	-	22.8	1.30	H-24'/C-23'; H-24'/C-25'
25'	14.2	14.2	0.88 (t)	H-25'/C-24'

1. Compound 2

Amorphous solid. IR ν_{max} (KBr) cm^{-1}: 3391 (O-H); *MS* spectrum showed the $[M]^+$ ion peak at *m/z* = 270 corresponded to $C_{13}H_{18}O_6$ (MW = 270), there also had a peak with *m/z* = 91 (tropylium ion). ^{1}H-NMR ($CDCl_3$+ CD_3OD, δ ppm): 7.3 - 7.4 (5H, m, protons of aromatic ring), 4.91 (1H, d, J = 11.5 Hz, -O-C**H**$_a$H-phenyl), 4.67 (1H, d, J = 12.0 Hz, -O-CH**H**$_b$-phenyl), 4.40 (1H, d, J = 7.5 Hz, H-1'); 3.90 - 3.36 (-C**H**-OH of glucose). ^{13}C-NMR and DEPT-NMR ($CDCl_3$+ CD_3OD, δ ppm): 137.3 (C1); 128.6 (C2 and C6); 128.3 (C3 and C5); 128.1 (C4); 102.2 (O-**C**H-O, C-1'), 76.62 (C-3'); 76.12 (C-5'); 73.79 (C-2'); 71.49 (C-4'), 70.37 (-O-**C**H_2-phenyl), 62.00 (-**C**H_2-OH, C6').

2. Compound 3

White powder. m.p. 144°C, IR ν_{max} (KBr) cm^{-1}: 3414 (O-H), 1662 (C=O amide); ^{1}H-, ^{13}C-NMR, HSQC, HMBC ($CDCl_3$+CD_3OD, δppm), were presented in table 1, figure 2 and appendix 1.

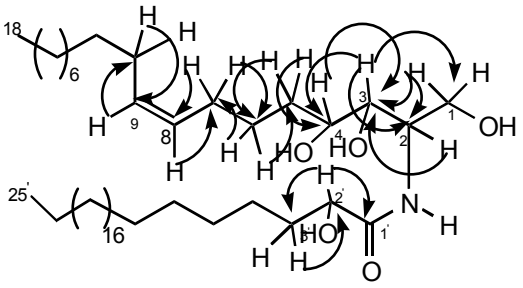

Figure 2: HMBC correlations of **3**

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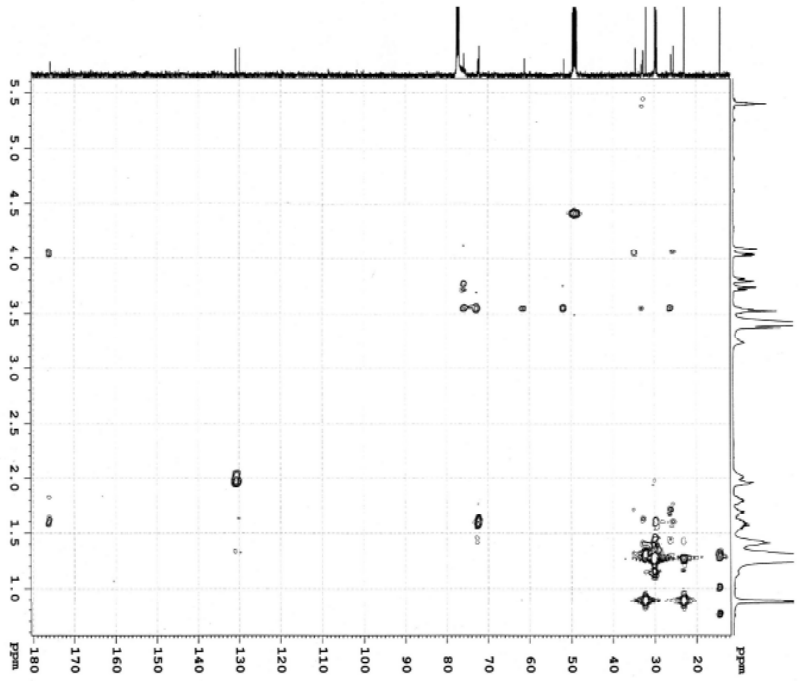
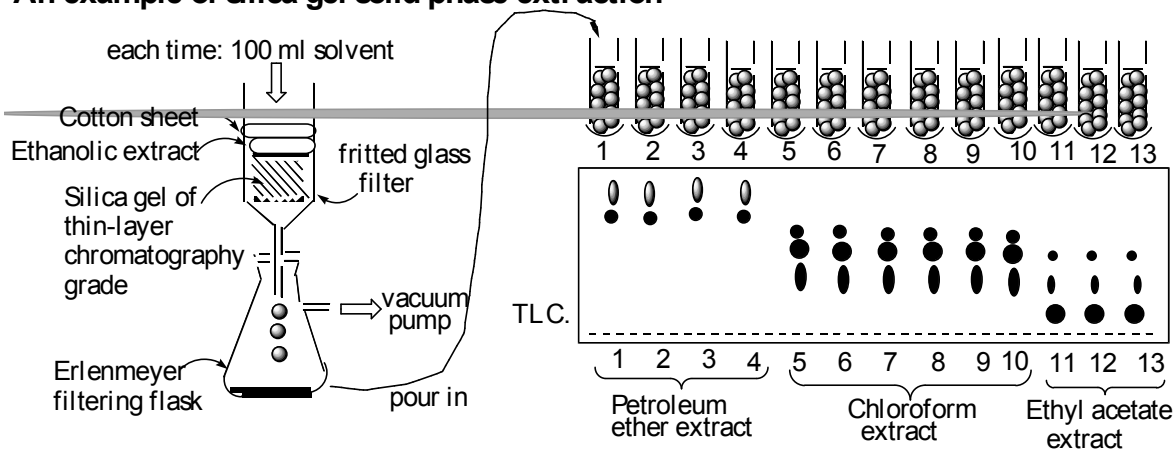


Appendix 1: The HMBC spectra of **3**

An example of silica gel solid phase extraction



In a fritted glass filter, silica gel of thin-layer chromatography grade was loaded into a layer of 5 cm height. The ethanolic extract was loaded onto the surface of the silica gel. The fritted glass filter was fitted onto an Erlenmeyer filtering flask that was jointed to a vacuum pump. Each time, a portion of 100 ml solvent was pour into the fritted glass filter, and the pump was on to *suck dried*, then the eluted solvent in the Erlenmeyer filtering flask was poured into a tube that was numbered. Another new elution was continued in the same manner. The tubes that had the same result of the thin-layer chromatography were grouped together, evaporated and gave a kind of fraction. The solvent was changed from petroleum ether, chloroform, ethyl acetate and methanol to give corresponding extracts.

Khảo sát hóa học lá cây Ninh lang Polyscias serrata Balf., họ Nhân sâm (Araliaceae)