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J. Nat. Prod., **1992**, 55 (4), 503-505• DOI:
10.1021/np50082a018 • Publication Date (Web): 01 July 2004

Journal of Natural Products
Vol. 55, No. 4, pp. 503-505, April 1992

AN ACETYLATED BIDESMOSIDIC SAPONIN FROM *SCHEFFLERA OCTOPHYLLA*

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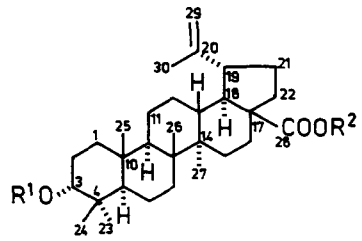
ABSTRACT.—A new acetylated bidesmosidic triterpenoid saponin has been isolated from the leaves of *Schefflera octophylla* and structurally elucidated as 3-*epi*-betulinic acid 3-*O*-β-D-6′-acetylglucopyranoside 28-[α-L-rhamnopyranosyl(1↦4)-*O*-β-D-glucopyranosyl(1↦6)]-β-D-glucopyranoside [**1**].

Schefflera octophylla (Lour.) Harms (Araliaceae) is used in Vietnamese folk medicine as an antirheumatic agent, a tonic drug, and a treatment for liver diseases (1). In earlier papers (2–5), several triterpenes and triterpenoid saponins from the leaves of this plant were reported. We now describe the isolation and structure elucidation of a new acetylated bidesmosidic saponin, 3-*epi*-betulinic acid 3-*O*-β-D-6′-acetylglucopyranoside 28-[α-L-rhamnopyranosyl(1↦4)-*O*-β-D-glucopyranosyl(1↦6)]-β-D-glucopyranoside [**1**] from the same source.

Repeated flash chromatography on Si gel of an MeOH extract of the leaves of *S. octophylla* followed by passage through Sephadex LH 20 and Lichroprep RP 18 columns afforded saponin **1** in 0.027% yield. The fabms spectrum of **1** showed peaks at *m/z* 1261.6 $[M + \text{thioglycerol}]^+$, 1153.6 $[M]^+$, and 682.4 $[M - \text{rha} - \text{glc} - \text{glc}]^+$. The presence of an additional acetyl group in **1** was indicated by a signal at 2.03 ppm in the ^{1}H-nmr spectrum as well as two signals at δ 20.77 and 172.77 ppm in the ^{13}C-nmr spectrum when compared with saponin **2** recently isolated from this plant (6). Alkaline hydrolysis of **1** yielded the glycoside **3**, while acid hydrolysis gave 3-*epi*-betulinic acid [**4**], identified by comparison of tlc and ir and ^{1}H-nmr spectra with authentic samples.

The position of the acetyl group in **1** was determined by analysis of the ^{13}C-nmr spectra of **1** and **2**. It has been reported (7,8) that on acetylation of an alcohol a methine carbon is deshielded and signals of carbons of β-positions are displaced upfield. Comparison of the ^{13}C-nmr spectrum of **1** with that of **2** (Table 1) showed that the C-5′ signal was displaced upfield by 3.11 ppm, whereas C-6′ was deshielded by 1.93 ppm. The other signals remained almost unaffected. This indicated that the acetyl group in **1** is located at C-6′. Thus, **1**



1 R^1=β-D-6-acetylglc′, R^2=β-D-glc″(1↦6)-β-D-glc‴(1↦4)-α-L-rha
2 R^1=β-D-glc′, R^2=β-D-glc″(1↦6)-β-D-glc‴(1↦4)-α-L-rha
3 R^1=β-D-glc, R^2=H
4 R^1=R^2=H

TABLE 1. ^{13}C-nmr Spectral Data of Compounds **1** and **2**.[a]

Carbon		Compound		Carbon		Compound
		1	**2**			**1**
C-1		35.32		C-17		57.99
C-2		21.93		C-18		50.57
C-3		83.16	82.5	C-19		48.36
C-4		38.35		C-20		151.79
C-5		51.24		C-21		31.55
C-6		19.25		C-22		37.61
C-7		34.49		C-23		29.18
C-8		42.19		C-24		22.98
C-9		50.98		C-25		16.86
C-10		38.05		C-26		16.70
C-11		22.19		C-27		15.31
C-12		26.84		C-28		176.34
C-13		39.38		C-29		110.39
C-14		43.68		C-30		19.53
C-15		30.86		$OCOCH_3$		20.77
C-16		32.85		$OCOCH_3$		172.77
Glc′	1	101.86	101.5	Glc‴	1	104.51
	2	75.29			2	75.02
	3	78.27			3	76.86
	4	72.04			4	78.02
	5	74.99	78.1		5	76.69
	6	64.83	62.9		6	61.91
Glc″	1	95.25		Rha	1	102.89
	2	73.74			2	72.42
	3	79.54			3	72.21
	4	70.96			4	73.98
	5	78.24			5	70.64
	6	69.54			6	17.84

[a]Data for **2** are from Sung *et al.* (6). Only the parameters that differed from those of **1** are shown for **2**.

was identified as 3-*epi*-betulinic acid 3-*O*-β-D-6′-acetylglucopyranoside 28-[α-L-rhamnopyranosyl(1↦4)-*O*-β-D-glucopyranosyl(1↦6)]-β-D-glucopyranoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's are uncorrected. Ir spectra were recorded on a Perkin-Elmer 1420. Fabms: Kratos, thioglycerol as matrix. ^{1}H-nmr spectra were recorded with Bruker AC 500 (500 MHz), and ^{13}C-nmr spectra with Bruker WM 500 (125.7) instruments in CD_3OD. Tlc employed precoated Si gel plates 60 F_{254} (Merck). Spray reagent: vanillin/H_2SO_4. Sephadex LH 20: Pharmacia Uppsala, Sweden; Lobar Fertigsäule Chroprep RP 18 (Merck).

PLANT MATERIAL.—The plant material used was collected in Nghe linh province, Vietnam in the spring of 1989 and identified as *S. octophylla* by Dr. P.V. Nguyen, Institute of Biology in Hanoi. A voucher specimen was deposited in the herbarium of this institute.

ISOLATION.—Dried leaves of *S. octophylla* (250 g) were extracted with $CHCl_3$ (1 liter) and then with MeOH (1 liter) in a Soxhlet apparatus. The residue of the MeOH extract was flash chromatographed on Si gel. Fractions eluted with $CHCl_3$-MeOH-H_2O (70:30:3) were successively purified on Sephadex LH 20 and RP 18 (solvent MeOH) to give **1** (67.5 mg, 0.027% yield) and the known saponin **2**.

Saponin **1**.—White powder: mp 230–235° (dec); $[\alpha]^{21}D$ −37° (*c* = 1.68, MeOH); ir ν max (KBr) 3420, 1730, 1640, 1250, 1030, 880 cm^{-1}; fabms *m/z* $[M + thioglycerol]^+$ 1261.6, $[M]^+$ 1153.6, $[M - CH_2CO]^+$ 1111.5, $[M - rha]^+$ 1007.5, $[M - rha - glc - glc]^+$ 682.4; ^{1}H nmr 0.83, 0.87, 0.89, 0.95, 1.02 and 1.69 (each 3H, s, tert Me), 1.26 (3H, d, *J* = 7 Hz, rha-Me), 2.04 (3H, s OAc), 3.00 (1H, dt, *J* = 11.8, 5.2 Hz, H-19), 4.24 (1H, d, *J* = 7.8 Hz, H-1′), 4.38 (1H, d, *J* = 7.8 Hz, H-1‴), 4.60 and 4.72

(each 1H, br s, H_2-29), 5.46 (1H, d, J = 7.8 Hz, H-1″); ^{13}C nmr see Table 1.

ALKALINE HYDROLYSIS OF **1**.—A solution of **1** (15 mg) in 5% methanolic KOH (3 ml) was heated at 80° for 4 h. The mixture was treated with Dowex 50 W × 4 (H^+ form) and evaporated. The residue was dissolved in H_2O and extracted with *n*-BuOH. The residue of the *n*-BuOH extract showed the presence of compound **3**.

ACID HYDROLYSIS OF **1**.—Compound **1** (10 mg) was hydrolyzed with 5% HCl (2 ml) at 80° for 4 h. The mixture was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ extract afforded 3-*epi*-betulinic acid [**4**].

ACKNOWLEDGMENTS

The authors are grateful to Dr. J. Rainer, University of Bayreuth and Dr. A. Porzel, Institute of Plant Biochemistry in Halle/S. for the nmr spectra, as well as to Dr. G. Eckhardt, University of Bonn, for the fabms. One of us (T.V. Sung) thanks the Alexander von Humboldt foundation for a research fellowship in the Institute of Organic Chemistry and Biochemistry, Bonn. This work was financially supported by the Ministry of Research and Technology, Germany.

LITERATURE CITED

1. Do Tat Loi, "Nhung cay thuoc va vi thuoc Viet Nam" (Glossary of Vietnamese Medicinal Plants), Nha Xuat ban K.H.K.T. (Science and Technics Publishing House), Hanoi, 1977, p. 817.
2. G. Adam, M. Lischewski, H.V. Phiet, A. Preiss, J. Schmidt, and T.V. Sung, *Phytochemistry*, **21**, 1385 (1982).
3. M. Lischewski, Ph.D. Ty, J. Schmidt, A. Preiss, H.V. Phiet, and G. Adam, *Phytochemistry*, **23**, 1695 (1984).
4. J. Kitajima and Y. Tanaka, *Chem. Pharm. Bull.*, **37**, 2727 (1989).
5. J. Kitajima, M. Shindo, and Y. Tanaka, *Chem. Pharm. Bull.*, **38**, 714 (1990).
6. T.V. Sung, J. Peter-Katalinic, and G. Adam, *Phytochemistry*, **30**, 3717 (1991).
7. K. Srivastava, *J. Nat. Prod.*, **52**, 1342 (1989).
8. K. Yamassaki, R. Kasai, Y. Masaki, M. Yokihara, O. Tanaka, H. Oshio, S. Takaga, M. Yamaki, K. Masuda, G. Nonaka, M. Tsubai, and D. Nishioka, *Tetrahedron Lett.*, 1231 (1977).

Received 22 May 1991