NEOVIBSANINS H AND I, NOVEL DITERPENES FROM *VIBURNUM AWABUKI*

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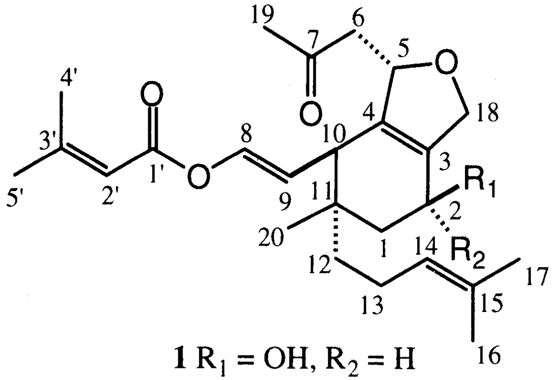
Neovibsanins H (**1**) and I (**2**), novel vibsane-type diterpenes, have been isolated from the leaves of *Viburnum awabuki* and their structures have been elucidated by spectroscopic analyses. The absolute configuration of **1** has been determined by applying the modified Mosher's method.

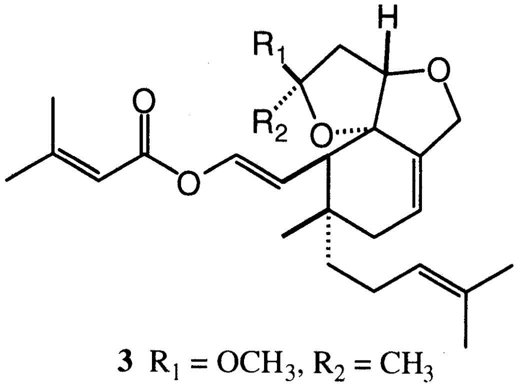
KEY WORDS *Viburnum awabuki*; Caprifoliaceae; neovibsanin H; neovibsanin I; vibsane-type diterpene; Mosher's method modified

In this communication, we report on the structure of novel vibsane-type[1)] diterpenes **1** and **2** named neovibsanins H and I, which are considered to be derived from a common biogenetic intermediate leading to neovibsanins A (**3**) and B (**4**).[2)] Neovibsanins H (11 mg) and I (2 mg) were isolated from the methanol extract (20 g) of the dried leaves of *Viburnum awabuki*.

Neovibsanin H (**1**)[3)] has the molecular formula $C_{25}H_{36}O_5$ as established by high–resolution FABMS, indicating eight degrees of unsaturation. The spectral data (Table) of **1** revealed the presence of a hydroxy group (3439 cm^{-1}), a tertiary methyl group (δ_H 0.80; δ_C 24.5), a methyl ketone function [1728 cm^{-1}; δ_H 1.88 (*s*); δ_C 205.0 and 30.5], an oxymethylene (δ_C 74.7), a tetrasubstituted double bond [δ_C 135.1 (*s*) and 137.0 (*s*)], and a β,β-dimethylacryl group (*m/z* 83) which is commonly involved in the enol ester group of the vibsane-type diterpenes previously known.[4, 5)] In addition to the above fragments, detailed analysis of COSY and HMQC gave five partial structures **A** – **E**, as shown in boldface in Fig. 1 (A). The *E* double bond in the **D** part was confirmed from



1 $R_1 = OH, R_2 = H$
2 $R_1 = H, R_2 = OH$



3 $R_1 = OCH_3, R_2 = CH_3$
4 $R_1 = CH_3, R_2 = OCH_3$

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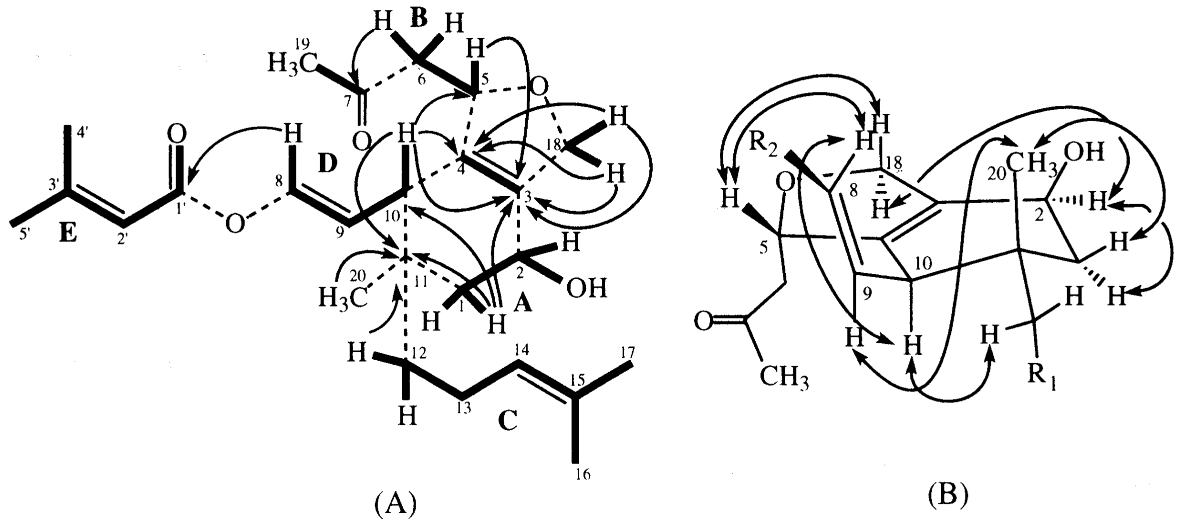

(A) (B)

Fig. 1. (A) Partial Structures **A** – **E** of **1** and Representative HMBC Correlations Denoted by Arrows and (B) Relative Stereochemistry of **1** Based on NOEs Indicated by Arrows

Table. ^{1}H and ^{13}C NMR Data (600 MHz, C_6D_6) of **1** and **2**

	1		**2**	
Carbon	^{13}C	^{1}H	^{13}C	^{1}H
1	40.9	1.29 (dd, 13.2, 7.3)	43.3	1.24 (*dd*, 12.7, 8.7)
		1.55 (dd, 13.2, 6.8)		1.62 (dd, 12.7, 5.6)
2	63.6	4.01 (dd, 7.3, 6.8)	63.8	3.91 (dd, 8.7, 5.6)
3	135.1		135.1	
4	137.0		136.3	
5	83.3	5.23 (dddd, 7.8, 4.2, 2.9, 2.4)	84.0	5.19 (brdd, 8.1, 3.5)
6	48.1	2.29 (dd, 14.4, 7.8)	47.9	2.37 (dd, 14.2, 8.1)
		2.37 (dd, 14.4, 4.2)		2.54 (dd, 14.2, 3.5)
7	205.0		205.2	
8	137.5	7.45 (d, 12.2)	138.6	7.44 (d, 12.5)
9	113.1	5.28 (dd, 12.2, 10.3)	111.2	5.14 (dd, 12.5, 11.2)
10	41.6	2.29 (dd, 10.3, 3.2)	42.0	2.58 (dd, 11.2, 2.4)
11	38.0		38.5	
12	38.9	1.19 (ddd, 13.6, 13.6, 5.4)	40.8	1.33 (ddd, 13.5, 13.5, 5.4)
		1.29 (ddd, 13.6, 13.6, 5.4)		1.36 (ddd, 13.5, 13.5, 5.4)
13	23.0	1.94 (dddd, 13.6, 13.6, 7.1, 5.4)	22.7	1.99 (m)
		1.95 (dddd, 13.6, 13.6, 7.1, 5.4)		2.04 (m)
14	125.2	5.19 (t, 7.1)	125.2	5.19 (t, 7.5)
15	131.1		131.1	
16	17.7	1.68 (3H, s)	17.7	1.68 (3H, s)
17	25.8	1.58 (3H, s)	25.8	1.62 (3H, s)
18	74.7	4.53 (ddd, 12.5, 3.2, 2.4)	74.6	4.52 (brd, 12.0)
		4.79 (dd, 12.5, 2.9)		4.87 (dd, 12.0, 2.4)
19	30.5	1.88 (3H, s)	30.8	1.92 (3H, s)
20	24.5	0.80 (3H, s)	20.5	0.62 (3H, s)
1'	163.2		163.1	
2'	115.1	5.65 (qq, 1.2, 1.2)	115.0	5.60 (qq, 1.2, 1.2)
3'	159.9		160.0	
4'	20.3	2.03 (3H, d, 1.2)	20.5	2.00 (3H, d, 1.2)
5'	27.0	1.36 (3H, d, 1.2)	27.0	1.34 (3H, d, 1.2)

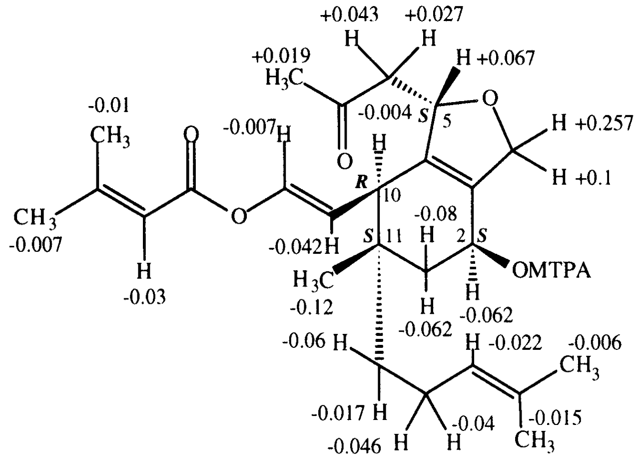

Fig. 2. $\Delta\delta = \delta_S - \delta_R$

significant NOE between H-8 and H-10 on 2D NOESY, and then the HMBC correlation of H-8 to C-1' led to the formation of an enol ester bond between the the β,β-dimethylacryl group **E** and the C-8 position of the **D** part in the same manner as neovibsanins A and B. Following the other HMBC correlations, which are shown by arrows in Fig. 1 (A), allowed us to propose the plane structure **1**, which could well explain homoallylic long-range couplings with 2.4 Hz and 2.9 Hz between H-5 and H-18 as well as with 3.2 Hz between H-10 and H-18. The relative stereochemistry of **1** was defined by a NOESY experiment, as shown in Fig. 1 (B). In order to determine the absolute configuration at C-2 of neovibsanin H (**1**), both the *R*- and *S*-MTPA esters were prepared. The $\Delta\delta$ values ($\delta_S - \delta_R$) of each ^{1}H NMR signal of the *R*- and *S*-MTPA esters of **1**, which are illustrated in Fig. 2, led us to assign a 2*S* configuration.[6)] Thus, the absolute configurations for the remaining chiral carbons of **1** were determined to be 5*S*, 10*R*, and 11*S*.

Neovibsanin I (**2**)[7)] has the same molecular formula as that of **1**. The ^{1}H and ^{13}C NMR data (Table) are also very similar to those of **1**. Moreover, 2D NMR experiments elaborated the spin systems associated with all the partial units presented in **1** and the HMBC of **2** made up of the same plane structure as **1**, suggesting that **2** is an epimer on the C-2 position in **1**. In contrast to the NOESY of **1**, the H-2 signal at δ_H 3.91 showed distinct cross–peaks to H_3-20 and H-18β. The above spectral data supported the epimeric nature of **2** on the C-2 position. Hence, the structure of neovibsanin I (**2**) was assigned as (2*R*)-**1**.

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3) **1**: $[\alpha]_D^{24}$ 81° (*c* 0.4, $CHCl_3$); HR-FABMS *m/z*: 439.2472 $[M+Na]^+$ (cacld for $C_{25}H_{36}O_5Na$: 439.2460); FABMS *m/z* (*rel. int.*): 439 $[M+Na]^+$, 83 (100); IR (FT) cm^{-1}: 3439 (OH), 1728 (C=O); λ_{max}^{EtOH}nm: 222 (ε 29000).
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7) **2**: $[\alpha]_D^{24}$ 28° (*c* 0.2, $CHCl_3$); HR-FABMS *m/z*: 439.2468 $[M+Na]^+$ (cacld for $C_{25}H_{36}O_5Na$: 439.2460); FABMS *m/z* (*rel. int.*): 439 $[M+Na]^+$, 83 (100); IR (FT) cm^{-1}: 3431 (OH), 1726 (C=O); λ_{max}^{EtOH}nm: 222 (ε 24000).

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