

Three New Lanostane Triterpenoids, Inonotsutriols A, B, and C, from *Inonotus obliquus*

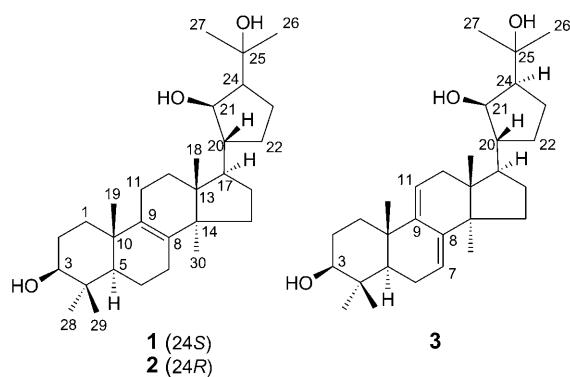
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Three new lanostane-type triterpenoids, inonotsutriols A (**1**), B (**2**), and C (**3**) were isolated from the sclerotia of *Inonotus obliquus* (PERS.: Fr.) (Japanese name: kabanoanatake; Russian name: chaga). Their structures were determined to be (3 β ,21*R*,24*S*)-21,24-cyclolanost-8-ene-3,21,25-triol (**1**), (3 β ,21*R*,24*R*)-21,24-cyclolanost-8-ene-3,21,25-triol (**2**), and (3 β ,21*R*,24*S*)-21,24-cyclolanosta-7,9(11)-diene-3,21,25-triol (**3**) on the basis of NMR spectroscopy including 1D and 2D experiments (¹H, ¹H-COSY, NOESY, HMQC, and HMBC) and EI-MS.

Introduction. – *Inonotus obliquus* (PERS.: Fr.) PIL. (= *Fuscoporia obliqua* (PERS.: Fr.) AOSHIMA), called kabanoanatake (in Japan) and chaga or tchaga (in Russia), is a white-rot fungus belonging to the family Hymenochaetaceae Donk [1], and the distribution of this mushroom is recognized in Europe, Asia, and North America [2]. The imperfect form of *I. obliquus* occurs parasitically on trunks, usually of *Betula* (birch), and more rarely also on *Ulmus*, *Alnus*, and *Fraxinus*. Only after the tree dies, the perfect form with pores and basidia is produced under the bark. *I. obliquus* is widely distributed in Hokkaido forests of *Betula platyphylla* var. *japonica* (Japanese name: shirakaba) in Japan [3][4]. Recently, several reports have been published concerning the biological activities of *I. obliquus* such as anticancer [5][6], including breast cancer [7], digestive disease [8][9], antioxidant [10][11], antimutation [12], anti-inflammatory [13], antioxidant and genoprotective [14], antibacterial, antiallergic, anti-inflammatory, and antioxidant activities [15], and platelet-aggregation inhibitory activity [16]. Recently, we reported the structures of five new lanostane-type triterpenoids isolated from the sclerotia: inonotsuoxides A and B ((3 β ,22*R*,24*S*)-22,25-epoxylanost-8-ene-3,24-diol and its (22*S*)-22,25-epoxy epimer) [17], and inonotsulides A, B, and C ((3 β ,20*R*,24*S*)-3,25-dihydroxylanost-8-en-20,24-olide, and its (20*R*,24*R*)-20,24-olide epimer, and (3 β ,20*R*,24*S*)-3,25-dihydroxylanosta-7,9(11)-dien-20,24-olide) [18] and the antitumor promoting activity of intodiol which is the most abundant triterpene in this sclerotia. Careful examination of the sclerotia of *I. obliquus* has led to the isolation of three new lanostane-type triterpenes named inonotsutriols A (**1**), B (**2**), and C (**3**). The structures of the new compounds **1–3** were determined on the basis of NMR spectroscopy, including 1D and 2D (¹H, ¹H-COSY, NOESY, HMQC, and HMBC) NMR, and EI-MS. Although Shin and co-workers isolated (3 β)-20,24-cyclolanost-8-ene-3,21,25-triol and determined its planar structure, its absolute config-



uration was not described completely [19]. Therefore, this report examines the absolute structures of these components.

Results and Discussion. – Sclerotia of *I. obliquus* were extracted with CHCl_3 , and from this extract, the three new triterpenes **1**–**3** were separated by column chromatography (silica gel), medium-pressure liquid chromatography (MPLC), and high performance liquid chromatography (HPLC).

The molecular formula of compound **1** was assigned as $\text{C}_{30}\text{H}_{50}\text{O}_3$ (M^+ at m/z 458.3763) by HR-EI-MS. The IR spectrum showed an OH group ($\tilde{\nu}_{\text{max}}$ 3368 cm^{-1}). The ^1H - and ^{13}C -NMR ^1H , ^1H -COSY, NOE, and HMBC data (Table 1 and Fig. 1) established the structure of inonotsutriol A (**1**) as (3 β ,21*R*,24*S*)-21,24-cyclolanost-8-ene-3,21,25-triol.

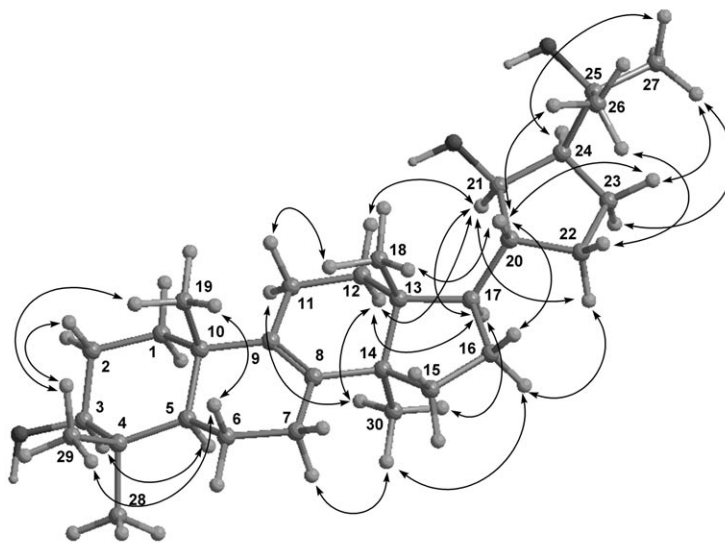


Fig. 1. Key NOE correlations for **1**

Table 1. ^1H and ^{13}C -NMR, $^1\text{H}/^1\text{H}$ -COSY, NOE, and HMBC ($\text{H} \rightarrow \text{C}$) Data of **1**. At 500 (^1H) and 125 (^{13}C) MHz in CDCl_3 ; δ in ppm, J in Hz.

	$\delta(\text{H})$	$^1\text{H}/^1\text{H}$ -COSY	NOE	$\delta(\text{C})$	HMBC
$\text{H}_\alpha\text{-C}(1)$	1.18–1.28 (<i>m</i>)	$\text{H}_\beta\text{-C}(1), \text{H}_\alpha\text{-C}(2), \text{H}_\beta\text{-C}(2)$	$\text{H-C}(3), \text{H-C}(5)$	35.6 (<i>t</i>)	$\text{C}(2)$
$\text{H}_\beta\text{-C}(1)$	1.70–1.78 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1), \text{H}_\alpha\text{-C}(2), \text{H}_\beta\text{-C}(2)$	$\text{CH}_2(11), \text{Me}(19)$		
$\text{H}_\alpha\text{-C}(2)$	1.64–1.71 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1), \text{H}_\beta\text{-C}(1), \text{H}_\beta\text{-C}(2)$	$\text{H-C}(3), \text{Me}(19), \text{Me}(29)$	27.9 (<i>t</i>)	$\text{C}(1), \text{C}(3)$
$\text{H}_\beta\text{-C}(2)$	1.54–1.63 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1), \text{H}_\beta\text{-C}(1), \text{H}_\alpha\text{-C}(2), \text{H-C}(3)$	$\text{H-C}(3), \text{Me}(19), \text{Me}(29)$		
$\text{H-C}(3)$	3.23 (<i>ddd, J = 11.7, 4.6</i>)	$\text{H}_\alpha\text{-C}(2), \text{H}_\beta\text{-C}(2)$	$\text{H-C}(5), \text{Me}(28)$	79.0 (<i>d</i>)	$\text{C}(2), \text{C}(4), \text{C}(28), \text{C}(29)$
$\text{C}(4)$				38.9 (<i>s</i>)	
$\text{H-C}(5)$	1.05 (<i>ddd, J = 11.7, 2.1</i>)	$\text{H}_\alpha\text{-C}(6), \text{H}_\beta\text{-C}(6)$	$\text{H}_\alpha\text{-C}(1), \text{H-C}(3), \text{H}_\alpha\text{-C}(6), \text{H}_\alpha\text{-C}(7), \text{Me}(28)$	50.4 (<i>d</i>)	$\text{C}(4), \text{C}(6), \text{C}(7), \text{C}(10), \text{C}(19)$
$\text{H}_\alpha\text{-C}(6)$	1.64–1.72 (<i>m</i>)	$\text{H-C}(5), \text{H}_\beta\text{-C}(6), \text{CH}_2(7)$	$\text{Me}(28)$	18.2 (<i>t</i>)	$\text{C}(4), \text{C}(5), \text{C}(10)$
$\text{H}_\beta\text{-C}(6)$	1.46–1.57 (<i>m</i>)	$\text{H-C}(5), \text{H}_\alpha\text{-C}(6), \text{CH}_2(7)$	$\text{Me}(19), \text{Me}(29)$	26.5 (<i>t</i>)	$\text{C}(8)$
$\text{CH}_2(7)$	2.01–2.08 (<i>m</i>)	$\text{H}_\alpha\text{-C}(6), \text{H}_\beta\text{-C}(6)$	$\text{H-C}(5), \text{Me}(30)$	134.3 (<i>s</i>)	
$\text{C}(8)$				134.6 (<i>s</i>)	
$\text{C}(9)$				37.1 (<i>s</i>)	
$\text{C}(10)$				20.9 (<i>t</i>)	
$\text{CH}_2(11)$	1.98–2.07 (<i>m</i>)	$\text{H}_\alpha\text{-C}(12), \text{H}_\beta\text{-C}(12)$	$\text{H}_\beta\text{-C}(1), \text{H}_\alpha\text{-C}(12), \text{H}_\beta\text{-C}(12), \text{Me}(18), \text{Me}(19), \text{Me}(30)$	29.0 (<i>t</i>)	$\text{C}(13)$
$\text{H}_\alpha\text{-C}(12)$	1.64–1.73 (<i>m</i>)	$\text{CH}_2(11), \text{H}_\beta\text{-C}(12)$	$\text{CH}_2(11), \text{H-C}(21)$		
$\text{H}_\beta\text{-C}(12)$	1.83–1.92 (<i>m</i>)	$\text{CH}_2(11), \text{H}_\alpha\text{-C}(12)$	$\text{CH}_2(11), \text{Me}(18), \text{H-C}(21)$	44.5 (<i>s</i>)	
$\text{C}(13)$				49.4 (<i>s</i>)	
$\text{C}(14)$				30.8 (<i>t</i>)	$\text{C}(14), \text{C}(16), \text{C}(30)$
$\text{H}_\alpha\text{-C}(15)$	1.15–1.23 (<i>m</i>)	$\text{H}_\beta\text{-C}(15), \text{H}_\alpha\text{-C}(16), \text{H}_\beta\text{-C}(16)$	$\text{H}_\alpha\text{-C}(6), \text{Me}(30)$		
$\text{H}_\beta\text{-C}(15)$	1.58–1.67 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15), \text{H}_\alpha\text{-C}(16), \text{H}_\beta\text{-C}(16)$	$\text{H}_\beta\text{-C}(16), \text{Me}(18)$		
$\text{H}_\alpha\text{-C}(16)$	1.79–1.88 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15), \text{H}_\beta\text{-C}(15), \text{H}_\beta\text{-C}(16), \text{H-C}(17)$	$\text{H}_\alpha\text{-C}(15), \text{H}_\alpha\text{-C}(22), \text{Me}(30)$	26.5 (<i>t</i>)	$\text{C}(15), \text{C}(17), \text{C}(20)$
$\text{H}_\beta\text{-C}(16)$	1.33–1.42 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15), \text{H}_\beta\text{-C}(15), \text{H}_\alpha\text{-C}(16), \text{H-C}(17)$	$\text{H}_\beta\text{-C}(15), \text{H-C}(17), \text{Me}(18), \text{H-C}(20), \text{H}_\beta\text{-C}(22)$		
$\text{H-C}(17)$	1.75–1.84 (<i>m</i>)	$\text{H}_\alpha\text{-C}(16), \text{H}_\beta\text{-C}(16), \text{H-C}(20)$	$\text{H}_\beta\text{-C}(16), \text{H-C}(21), \text{H}_\alpha\text{-C}(22), \text{Me}(30)$	49.0 (<i>d</i>)	$\text{C}(13), \text{C}(16), \text{C}(20), \text{C}(21)$
$\text{Me}(18)$	0.73 (<i>s</i>)		$\text{CH}_2(11), \text{H}_\beta\text{-C}(12), \text{H}_\beta\text{-C}(15), \text{H}_\beta\text{-C}(16), \text{Me}(19), \text{H-C}(20)$	15.4 (<i>q</i>)	$\text{C}(12), \text{C}(13), \text{C}(14), \text{C}(17)$

Table 1 (cont.)

	$\delta(\text{H})$	$^1\text{H}-^1\text{H-COSY}$	NOE	$\delta(\text{C})$	HMBC
Me(19)	0.97 (s)		H $_{\beta}$ -C(1), H $_{\beta}$ -C(2), H $_{\beta}$ -C(6), CH $_2$ (11), Me(18), Me(29)	19.1 (q)	C(1), C(5), C(9), C(10)
H-C(20)	1.82–1.92 (m)	H-C(17), H-C(21), H $_{\alpha}$ -C(22), H $_{\beta}$ -C(22)	H $_{\beta}$ -C(16), Me(18), H-C(21), H $_{\beta}$ -C(22), H $_{\beta}$ -C(23), Me(26)	47.8 (d)	C(17), C(21), C(22)
H-C(21)	3.72 (dd, $J=8.7, 7.3$)	H-C(20), H-C(24)	H $_{\alpha}$ -C(12), H $_{\beta}$ -C(12), H-C(17), H $_{\alpha}$ -C(22), H-C(24), Me(27)	79.1 (d)	C(17), C(25)
H $_{\alpha}$ -C(22)	1.17–1.26 (m)	H-C(20), H $_{\beta}$ -C(22), H $_{\alpha}$ -C(23), H $_{\beta}$ -C(23)	H-C(17), H-C(21), H $_{\alpha}$ -C(23)	24.5 (t)	C(20), C(21)
H $_{\beta}$ -C(22)	1.63–1.72 (m)	H-C(20), H $_{\alpha}$ -C(22)	H-C(20), Me(26)		
H $_{\alpha}$ -C(23)	1.30–1.40 (m)	H $_{\alpha}$ -C(22), H $_{\beta}$ -C(23), H-C(24)	H $_{\alpha}$ -C(20), Me(27)	27.4 (t)	C(20), C(22), C(24)
H $_{\beta}$ -C(23)	1.77–1.86 (m)	H $_{\alpha}$ -C(22), H $_{\alpha}$ -C(23), H-C(24)	H-C(20), H-C(24), Me(27)		
H-C(24)	1.85–1.94 (m)	H-C(21), H $_{\alpha}$ -C(23), H $_{\beta}$ -C(23)	H-C(21), H $_{\beta}$ -C(23), Me(27)	57.6 (d)	C(21), C(25)
C(25)				73.5 (s)	
Me(26)	1.20 ^{a)} (s)		H-C(20), H $_{\beta}$ -C(22)	24.1 (q)	C(24), C(25), C(27)
Me(27)	1.23 ^{a)} (s)		H $_{\alpha}$ -C(23), H $_{\beta}$ -C(23)	30.7 (q)	C(24), C(25), C(26)
Me(28)	1.00 (s)		H-C(3), H-C(5), H $_{\alpha}$ -C(6)	28.0 (q)	C(3), C(4), C(5), C(29)
Me(29)	0.81 (s)		H $_{\beta}$ -C(2), H $_{\beta}$ -C(6), Me(19)	17.0 (q)	C(3), C(4), C(5), C(28)
Me(30)	0.90 (s)		CH $_2$ (7), CH $_2$ (11), H $_{\alpha}$ -C(12), H $_{\alpha}$ -C(15), H $_{\alpha}$ -C(16), H-C(17)	24.4 (q)	C(8), C(13), C(14), C(15)

^{a)} Assignments may be reversed.

The ^1H - and ^{13}C -NMR spectra (CDCl_3) of **1** (Table 1) exhibited signals of seven Me, ten CH_2 , and six sp^3 CH groups, including two oxymethines ($\delta(\text{H})$ 3.23 (*dd*, $J = 11.7, 4.6$ Hz); $\delta(\text{C})$ 79.0 (*d*)); $\delta(\text{H})$ 3.72 (*dd*, $J = 8.7, 7.3$ Hz); $\delta(\text{C})$ 79.1 (*d*)), five sp^3 quaternary C-atoms including one OH group ($\delta(\text{C})$ 73.5 (*s*)), and a tetrasubstituted C=C bond ($\delta(\text{C})$ 134.3 and 134.6 (*2s*)). The planar structure of **1** was determined by HMBC and $^1\text{H}, ^1\text{H}$ -COSY experiments. The HMBC data of **1** (Table 1 and Fig. 1) indicated the long-range correlations Me(18) ($\delta(\text{H})$ 0.73)/C(12), C(13), C(14), and C(17), Me(19) ($\delta(\text{H})$ 0.97)/C(1), C(5), C(9), and C(10), Me(26) ($\delta(\text{H})$ 1.20)/C(24), C(25), and C(27), Me(27) ($\delta(\text{H})$ 1.23)/C(24), C(25), and C(26), Me(28) ($\delta(\text{H})$ 1.00)/C(3), C(4), C(5), and C(29), Me(29) ($\delta(\text{H})$ 0.81)/C(3), C(4), C(5), and C(28), and Me(30) ($\delta(\text{H})$ 0.90)/C(8), C(13), C(14), and C(15). In the $^1\text{H}, ^1\text{H}$ -COSY plot (Table 1), the following correlations were observed: H–C(20) ($\delta(\text{H})$ 1.82–1.92)/H–C(17) ($\delta(\text{H})$ 1.75–1.84), H–C(21) ($\delta(\text{H})$ 3.72), and CH_2 (22) ($\delta(\text{H})$ 1.17–1.26 and 1.63–1.72), H–C(21)/H–C(20) and H–C(24), H–C(24)/H–C(21) and CH_2 (23) ($\delta(\text{H})$ 1.30–1.40 and 1.77–1.86). The molecular formula of $\text{C}_{30}\text{H}_{50}\text{O}_3$ and the spectral data mentioned above suggested that the structure of **1** was a (3β)-lanost-8-en-3,21,25-triol having a cyclopentane ring between C(20) and C(24) in the side chain. The configuration at the cyclopentane-ring members C(20) and C(24) was established as ($20R$) and ($24S$) because significant NOEs were observed from H–C(20) to H_β -C(16), Me(18), H_β -C(23), and Me(26), from H_α -C(24) to Me(27), from Me(26) to H_β -C(20) and H_β -C(22), and from Me(27) to CH_2 (23) and H_α -C(24), indicating the ($20R, 24S$)-configuration. One of the OH groups was in β -position at C(3) as shown by the chemical shift and the coupling constants ($\delta(\text{H})$ 3.23 (*dd*, $J(3,2\alpha) = 4.6$ Hz and $J(3,2\beta) = 11.7$ Hz, H–C(3)); $\delta(\text{C})$ 79.0 (*d*)). The configuration at the other secondary, OH-substituted center C(21) was determined as ($21R$) because the significant NOEs H–C(21)/ CH_2 (12), H_α -C(17), H_α -C(22), H_α -C(24), and Me(27) and coupling constants ($\delta(\text{H})$ 3.72 (*dd*, $J(21,20) = 8.7$ Hz and $J(21,24) = 7.3$ Hz, H–C(21))) were observed. Other NOEs were observed, *i.e.*, Me(29)/ H_β -C(2), H_β -C(6), and Me(19), H_α -C(5)/ H_α -C(7), H_β -C(6)/Me(19) and Me(29), H_α -C(7)/Me(30), H_α -C(12)/ H_α -C(17), H–(21), and Me(30), and H_β -C(11)/Me(18). Therefore, the rings A, B, and C in **1** adopted a chair, half-chair, and half-chair conformation, respectively (Fig. 1).

The minor compound **2** had the same molecular formula $\text{C}_{30}\text{H}_{50}\text{O}_3$ (M^+ at m/z 458.3759) as **1** by HR-EI-MS. The IR, ^1H - and ^{13}C -NMR, HMBC, and $^1\text{H}, ^1\text{H}$ -COSY data (Table 2) resembled those of **1** and allowed, together with the NOE data (Fig. 2), to establish the structure of inonotsutriol B (**2**) as ($3\beta, 21R, 24R$)-21,24-cyclolanost-8-ene-3,21,25-triol, which is a C(24) epimer of **1**.

Differences between the NMR data of **1** and **2** were observed for H–C(17) ($\delta(\text{H})$ 1.65–1.74), H–C(20) ($\delta(\text{H})$ 1.70–1.88), H–C(21) ($\delta(\text{H})$ 3.76), Me(18) ($\delta(\text{H})$ 0.69), and Me(26) ($\delta(\text{H})$ 1.21) and C(12) ($\delta(\text{C})$ 30.6), C(17) ($\delta(\text{C})$ 50.5), C(18) ($\delta(\text{C})$ 16.4), C(20) ($\delta(\text{C})$ 48.9), C(21) ($\delta(\text{C})$ 81.4), and C(24) ($\delta(\text{C})$ 56.0). The configuration at C(20) and C(24) of the cyclopentane moiety was established as ($20R$) and ($24R$) because significant NOEs were observed from H–C(20) to H_β -C(16), Me(18), H_β -C(23), and H–C(24), and from H–C(24) to H–C(20), Me(26), and Me(27). The configuration at the OH-substituted C(21) was determined as ($21R$), the same as in **1** because of the significant NOEs H–C(21)/ H_α -C(17), H_α -C(22), H_α -C(23), Me(26), and Me(27) and of the coupling constants ($\delta(\text{H})$ 3.76 (*t*, $J(21,20) = J(21,24) = 8.7$ Hz, H–C(21))) see (Fig. 2).

Compound **3** had the molecular formula $\text{C}_{30}\text{H}_{48}\text{O}_3$ (M^+ at m/z 456.3607) by HR-EI-MS. The IR and UV spectra showed OH groups ($\tilde{\nu}_{\text{max}}$ 3675 cm^{-1}) and a heteroannular diene moiety (λ_{max} 232, 237, and 245 (ϵ 12000, 14500, and 9000, resp.)). The ^1H - and ^{13}C -NMR, $^1\text{H}, ^1\text{H}$ -COSY, NOE, and HMBC data (Table 3 and Fig. 3) established the structure of inonotsutriol C (**3**) as ($3\beta, 21R, 24S$)-21,24-cyclolanosta-7,9(11)-diene-3,21,25-triol.

Table 2. ^1H and ^{13}C -NMR, ^1H , ^1H -COSY, NOE, and HMBC (H \rightarrow C) Data of **2**. At 500 (^1H) and 125 (^{13}C) MHz in CDCl_3 ; δ in ppm, J in Hz.

	$\delta(\text{H})$	^1H , ^1H -COSY	NOE	$\delta(\text{C})$	HMBC
$\text{H}_\alpha\text{-C}(1)$	1.18–1.27 (<i>m</i>)	$\text{H}_\beta\text{-C}(1)$, $\text{H}_\alpha\text{-C}(2)$, $\text{H}_\beta\text{-C}(2)$	$\text{H}_\alpha\text{-C}(2)$, $\text{H-C}(3)$, $\text{H-C}(5)$, $\text{H}_\alpha\text{-C}(12)$, $\text{Me}(30)$	35.6 (<i>t</i>)	$\text{C}(2)$, $\text{C}(3)$, $\text{C}(5)$, $\text{C}(9)$, $\text{C}(10)$, $\text{C}(19)$
$\text{H}_\beta\text{-C}(1)$	1.69–1.76 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\alpha\text{-C}(2)$, $\text{H}_\beta\text{-C}(2)$	$\text{Me}(30)$		
$\text{H}_\alpha\text{-C}(2)$	1.63–1.72 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\beta\text{-C}(1)$, $\text{H}_\beta\text{-C}(2)$, $\text{H-C}(3)$	$\text{H}_\alpha\text{-C}(1)$, $\text{H-C}(3)$	27.8 (<i>t</i>)	$\text{C}(3)$, $\text{C}(4)$, $\text{C}(10)$
$\text{H}_\beta\text{-C}(2)$	1.54–1.62 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\beta\text{-C}(1)$, $\text{H}_\alpha\text{-C}(2)$, $\text{H-C}(3)$	$\text{Me}(19)$, $\text{Me}(29)$		
$\text{H-C}(3)$	3.24 (<i>dd</i> , $J=11.7, 4.6$)	$\text{H}_\alpha\text{-C}(2)$, $\text{H}_\beta\text{-C}(2)$	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\alpha\text{-C}(2)$, $\text{H}_\beta\text{-C}(2)$, $\text{H-C}(5)$, $\text{Me}(28)$	79.0 (<i>d</i>)	$\text{C}(4)$, $\text{C}(28)$, $\text{C}(29)$
$\text{C}(4)$				38.9 (<i>s</i>)	
$\text{H-C}(5)$	1.05 (<i>dd</i> , $J=10.8, 2.1$)	$\text{H}_\alpha\text{-C}(6)$, $\text{H}_\beta\text{-C}(6)$	$\text{H}_\alpha\text{-C}(1)$, $\text{H-C}(3)$, $\text{CH}_2(7)$, $\text{H-C}(17)$, $\text{Me}(30)$	50.4 (<i>d</i>)	$\text{C}(4)$, $\text{C}(6)$, $\text{C}(7)$, $\text{C}(10)$, $\text{C}(19)$, $\text{C}(28)$, $\text{C}(29)$
$\text{H}_\alpha\text{-C}(6)$	1.65–1.72 (<i>m</i>)	$\text{H-C}(5)$, $\text{H}_\beta\text{-C}(6)$, $\text{CH}_2(7)$	$\text{Me}(28)$	18.2 (<i>t</i>)	$\text{C}(5)$, $\text{C}(7)$, $\text{C}(8)$, $\text{C}(10)$
$\text{H}_\beta\text{-C}(6)$	1.47–1.55 (<i>m</i>)	$\text{H-C}(5)$, $\text{H}_\alpha\text{-C}(6)$, $\text{CH}_2(7)$	$\text{CH}_2(7)$, $\text{CH}_2(11)$, $\text{Me}(18)$, $\text{Me}(19)$, $\text{Me}(29)$		
$\text{CH}_2(7)$	2.02–2.09 (<i>m</i>)	$\text{H}_\alpha\text{-C}(6)$, $\text{H}_\beta\text{-C}(6)$	$\text{H-C}(5)$, $\text{H}_\beta\text{-C}(6)$, $\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{Me}(30)$	26.5 (<i>t</i>)	$\text{C}(8)$, $\text{C}(9)$
$\text{C}(8)$				134.3 (<i>s</i>)	
$\text{C}(9)$				134.4 (<i>s</i>)	
$\text{C}(10)$				37.0 (<i>s</i>)	
$\text{CH}_2(11)$	1.95–2.05 (<i>m</i>)	$\text{H}_\alpha\text{-C}(12)$, $\text{H}_\beta\text{-C}(12)$	$\text{H}_\beta\text{-C}(6)$, $\text{H}_\alpha\text{-C}(12)$, $\text{Me}(18)$, $\text{Me}(19)$	20.9 (<i>t</i>)	
$\text{H}_\alpha\text{-C}(12)$	1.46–1.55 (<i>m</i>)	$\text{CH}_2(11)$, $\text{H}_\beta\text{-C}(12)$	$\text{H}_\alpha\text{-C}(1)$, $\text{CH}_2(11)$, $\text{H-C}(17)$	30.6 (<i>t</i>)	$\text{C}(13)$, $\text{C}(17)$, $\text{C}(18)$
$\text{H}_\beta\text{-C}(12)$	1.64–1.72 (<i>m</i>)	$\text{CH}_2(11)$, $\text{H}_\alpha\text{-C}(12)$	$\text{Me}(18)$, $\text{H-C}(21)$		
$\text{C}(13)$				45.4 (<i>s</i>)	
$\text{C}(14)$				48.6 (<i>s</i>)	
$\text{H}_\alpha\text{-C}(15)$	1.20–1.28 (<i>m</i>)	$\text{H}_\beta\text{-C}(15)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H}_\beta\text{-C}(16)$	$\text{Me}(30)$	31.4 (<i>t</i>)	$\text{C}(16)$, $\text{C}(30)$
$\text{H}_\beta\text{-C}(15)$	1.61–1.68 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H}_\beta\text{-C}(16)$	$\text{Me}(18)$		
$\text{H}_\alpha\text{-C}(16)$	1.68–1.77 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{H}_\beta\text{-C}(16)$, $\text{H-C}(17)$	$\text{H}_\alpha\text{-C}(22)$, $\text{Me}(30)$	26.5 (<i>t</i>)	$\text{C}(17)$
$\text{H}_\beta\text{-C}(16)$	1.92–2.00 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H-C}(17)$	$\text{H-C}(20)$, $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$		
$\text{H-C}(17)$	1.65–1.74 (<i>m</i>)	$\text{H}_\alpha\text{-C}(16)$, $\text{H}_\beta\text{-C}(16)$, $\text{H-C}(20)$	$\text{H}_\alpha\text{-C}(12)$, $\text{H-C}(21)$, $\text{Me}(30)$	50.5 (<i>d</i>)	$\text{C}(13)$, $\text{C}(18)$
$\text{Me}(18)$	0.69 (<i>s</i>)		$\text{H}_\beta\text{-C}(6)$, $\text{CH}_2(11)$, $\text{H}_\beta\text{-C}(15)$, $\text{Me}(19)$, $\text{H-C}(20)$	16.4 (<i>q</i>)	$\text{C}(12)$, $\text{C}(13)$, $\text{C}(14)$, $\text{C}(17)$

Table 2 (cont.)

	$\delta(\text{H})$	$^1\text{H}, ^1\text{H-COSY}$	NOE	$\delta(\text{C})$	HMBC
Me(19)	0.98 (s)		$\text{H}_\beta\text{-C}(2)$, $\text{H}_\beta\text{-C}(6)$, $\text{CH}_2(11)$, $\text{H}_\beta\text{-C}(15)$, Me(18), Me(23)	19.1 (q)	C(1), C(5), C(9), C(10)
H-C(20)	1.70–1.88 (m)	$\text{H}_\alpha\text{-C}(17)$, H-C(21), $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$	$\text{H}_\beta\text{-C}(16)$, Me(18), $\text{H}_\beta\text{-C}(23)$, H-C(24)	48.9 (d)	C(17), C(21)
H-C(21)	3.76 (t, $J = 8.7$)	H-C(20), H-C(24)	H-C(17), $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, Me(26), Me(27)	81.4 (d)	C(17), C(20), C(25)
$\text{H}_\alpha\text{-C}(22)$	1.17–1.26 (m)	H-C(20), H-C(22), $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	$\text{H}_\beta\text{-C}(16)$, H-C(21), $\text{H}_\beta\text{-C}(22)$	23.9 (t)	C(17), C(20), C(21)
$\text{H}_\beta\text{-C}(22)$	1.63–1.72 (m)	H-C(20), $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	$\text{H}_\beta\text{-C}(22)$ $\text{H}_\alpha\text{-C}(22)$		
$\text{H}_\alpha\text{-C}(23)$	1.30–1.40 (m)	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$, $\text{H}_\beta\text{-C}(23)$, H-C(24)	$\text{H}_\beta\text{-C}(16)$, H-C(21), $\text{H}_\beta\text{-C}(23)$	27.3 (t)	C(20), C(21), C(25), C(26), C(27)
$\text{H}_\beta\text{-C}(23)$	1.77–1.86 (m)	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, H-C(24)	H-C(20), $\text{H}_\alpha\text{-C}(23)$, Me(26), Me(27)		
H-C(24)	1.85–1.94 (m)	H-C(21), $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	H-C(20), Me(26), Me(27)	56.0 (d)	C(20), C(21), C(25), C(26), C(27)
C(25)				73.5 (s)	
Me(26)	1.21 ^a (s)		H-C(21), $\text{H}_\beta\text{-C}(23)$, H-C(24), Me(27)	30.3 ^a (q)	C(24), C(25), C(26)
Me(27)	1.21 ^a (s)		H-C(21), H-C(24), Me(26)	24.2 ^a (q)	C(24), C(25), C(26)
Me(28)	1.00 (s)		H-C(3), H-C(5), $\text{H}_\alpha\text{-C}(6)$	28.0 (q)	C(3), C(4), C(5), C(29)
Me(29)	0.81 (s)		$\text{H}_\beta\text{-C}(2)$, $\text{H}_\beta\text{-C}(6)$, $\text{H}_\beta\text{-C}(15)$, Me(19)	15.4 (q)	C(3), C(4), C(5), C(28)
Me(30)	0.89 (s)		$\text{H}_\alpha\text{-C}(1)$, H-C(5), $\text{CH}_2(7)$, H-C(17)	24.3 (q)	C(8), C(13), C(14), C(15)

^a) Assignments may be reversed.

The ^1H - and ^{13}C -NMR spectra of **3** resembled those of **1**, except for H-C(7) ($\delta(\text{H})$ 5.47, *d*), H-C(11) ($\delta(\text{H})$ 5.37, *d*) in the ^1H -NMR spectrum and C(7) ($\delta(\text{C})$ 120.0, *d*), C(8) ($\delta(\text{C})$ 142.9, *s*), C(9) ($\delta(\text{C})$ 145.9, *s*), and C(11) ($\delta(\text{C})$ 116.5, *s*) in the ^{13}C -NMR spectrum. The HMBC plot showed the long-range correlations Me(19) ($\delta(\text{H})$ 0.98)/C(9), Me(30) ($\delta(\text{H})$ 0.91)/C(8), $\text{H}_\alpha\text{-C}(5)$ ($\delta(\text{H})$ 1.09)/C(6) and C(7), and $\text{CH}_2(12)$ ($\delta(\text{H})$ 2.17 and 2.38)/C(11). The configuration at C(20) and C(24) of the cyclopentane moiety was established as (20*R*) and (24*S*) because significant NOEs were observed from H-C(20) to $\text{H}_\beta\text{-C}(16)$, Me(18), and $\text{H}_\beta\text{-C}(23)$, and from H-C(24) to H-C(21) and Me(27), which is same as that of **1** (Fig. 3). Other NOEs were H-C(7)/ $\text{CH}_2(6)$, $\text{CH}_2(15)$, and Me(30), H-C(11)/ $\text{CH}_2(1)$, $\text{CH}_2(12)$, and Me(19), $\text{H}_\alpha\text{-C}(3)$ / $\text{H}_\alpha\text{-C}(1)$, $\text{H}_\alpha\text{-C}(5)$, and Me(28), $\text{H}_\alpha\text{-C}(21)$ / $\text{CH}_2(12)$, $\text{H}_\alpha\text{-C}(17)$, $\text{H}_\beta\text{-C}(20)$, and Me(26), and $\text{H}_\beta\text{-C}(16)$ /Me(18), $\text{H}_\beta\text{-C}(20)$, $\text{H}_\beta\text{-C}(22)$, and Me(26) (Fig. 3).

It is suggested that compounds **1–3** are biosynthesized from (3 β)-3-hydroxylanosta-8,24-dien-21-al, which is the main triterpene constituent in these sclerotia (Scheme). Attack by the C(24)=C(25) bond on C(21)=O and the C–C bond-formation yields an

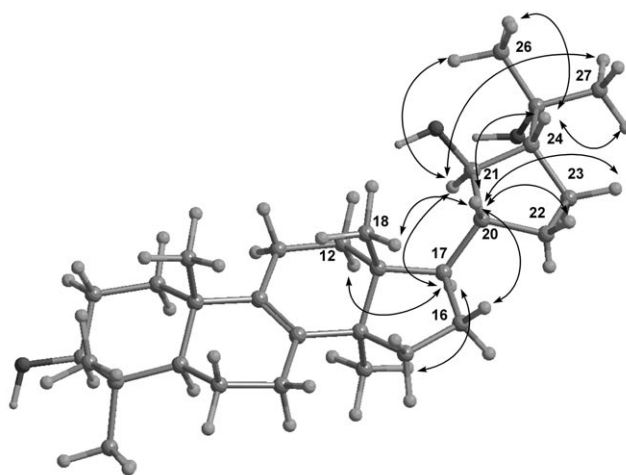


Fig. 2. Key NOE correlations for **2**

intermediate **a**, which then generates **1–3** by the attack of an OH^- -anion at C(25) of the cation.

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Experimental Part

General. Column chromatography (CC): silica gel (70–230 mesh, *Merck*). Medium-pressure liquid chromatography (MPLC): silica gel (230–400 mesh, *Merck*). HPLC: *Jasco-PU-1586* instrument equipped with a differential refractometer (*RI 1531*). Anal. TLC: silica gel 60 *F₂₅₄* (*Merck*). Prep. TLC: silica gel *F₂₅₄* plates (20 × 20 cm, 0.5 mm thick; *Merck*). M.p.: *Yanagimoto* micro-melting-point apparatus; uncorrected. Optical rotations: *Jasco-DIP-1000* digital polarimeter. UV Spectra: *Hitachi U-200*, λ_{max} (ϵ) in nm. IR Spectra: *Perkin-Elmer-1720X* FT-IR spectrophotometer; $\tilde{\nu}_{\text{max}}$ in cm^{-1} . ^1H - and ^{13}C -NMR Spectra: *Varian-INOVA-500* spectrometer with standard pulse sequences, at 500 and 125 MHz, resp.; CDCl_3 as the solvent and Me_4Si as the internal standard. EI-MS: *Hitachi-4000-H* double-focusing mass spectrometer (70 eV); in m/z (rel. %).

Material. *Inonotus obliquus* was successfully cultured by *Salada Melon Co., Ltd.*, Nayoro City, Hokkaido, Japan. Sclerotium (4 kg) of *Inonotus obliquus* was obtained in April, 2004 from this company.

Extraction and Isolation. The sclerotia of white-rot fungus, *Inonotus obliquus* (PERS. Fr.) PIL. (4 kg) was extracted with CHCl_3 (10 l) in 2005. Preliminary CC (silica gel (3 kg)) of the CHCl_3 extract (153.9 g) of the sclerotia of *I. obliquus* has been reported [18], with separation into *Fractions A–E*. The residue of *Fr. D* was recrystallized from $\text{MeOH}/\text{CHCl}_3$ to give trametenolic acid (10.9 g), and the filtrate (23.8 g) was subjected to CC (silica gel (1.5 kg)). Elution with $\text{CHCl}_3/\text{AcOEt}$ 5 : 1; (*Frs.* 76–89) gave a yellow residue *D1*, 1.85 g, and further elution with $\text{CHCl}_3/\text{AcOEt}$ 2 : 1; (*Frs.* 90–115) gave a yellow residue *D4* (3.25 g). Residue *D4* was subjected to MPLC (silica gel (100 g), hexane/ AcOEt 3 : 1) to give a crystalline residue *D5* (*Frs.* 61–68; 145.2 mg), which was separated by HPLC (*ODS*, 90% MeOH): **1** (65.9 mg), **2** (13.1 mg), and **3** (7.2 mg).

Inonotsutriol A (= (3 β ,21R,24S)-21,24-Cyclolanost-8-ene-3,21,25-triol = (3 β ,5 α ,17 β)-17-[1R,2R,3S)-2-Hydroxy-3-(1-hydroxy-1-methylethyl)cyclopentyl]-4,4,14-trimethylandrosta-8-en-3-ol; **1**): Colorless crystals. M.p. 203–205° (from $\text{MeOH}/\text{CHCl}_3$). $[\alpha]_{\text{D}}^{20} = +40.2$ ($c = 0.27$, CHCl_3). IR (KBr): 3368 (OH),

Table 3. ^1H - and ^{13}C -NMR, ^1H , ^1H -COSY, NOE, and HMBC ($\text{H} \rightarrow \text{C}$) Data of **3**. At 500 (^1H) and 125 (^{13}C) MHz in CDCl_3 ; δ in ppm, J in Hz.

	$\delta(\text{H})$	$^1\text{H}, ^1\text{H}$ -COSY	NOE	$\delta(\text{C})$	HMBC
$\text{H}_\alpha\text{-C}(1)$	1.45 (<i>td</i> , $J = 13.5, 4.2$)	$\text{H}_\beta\text{-C}(1)$, $\text{CH}_2(2)$	$\text{CH}_2(2)$, $\text{H-C}(3)$, $\text{H-C}(5)$, $\text{H-C}(11)$	35.8 (<i>t</i>)	$\text{C}(2)$, $\text{C}(3)$, $\text{C}(5)$, $\text{C}(9)$, $\text{C}(10)$, $\text{C}(19)$
$\text{H}_\beta\text{-C}(1)$	2.00 (<i>dt</i> , $J = 13.5, 4.2$)	$\text{H}_\alpha\text{-C}(1)$, $\text{CH}_2(2)$	$\text{CH}_2(2)$, $\text{H-C}(11)$, $\text{Me}(19)$		
$\text{CH}_2(2)$	1.63–1.74 (<i>m</i>)	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\beta\text{-C}(1)$, $\text{H-C}(3)$	$\text{Me}(30)$	27.8 (<i>t</i>)	$\text{C}(1)$, $\text{C}(3)$, $\text{C}(4)$, $\text{C}(10)$
$\text{H-C}(3)$	3.25 (<i>dd</i> , $J = 11.3, 4.2$)	$\text{CH}_2(2)$	$\text{H}_\alpha\text{-C}(1)$, $\text{CH}_2(2)$, $\text{H-C}(5)$, $\text{Me}(28)$	79.0 (<i>d</i>)	$\text{C}(28)$, $\text{C}(29)$
$\text{C}(4)$				38.7 (<i>s</i>)	
$\text{H-C}(5)$	1.09 (<i>dd</i> , $J = 10.8, 5.0$)	$\text{CH}_2(6)$	$\text{H}_\alpha\text{-C}(1)$, $\text{H-C}(3)$, $\text{H}_\alpha\text{-C}(6)$, $\text{Me}(28)$, $\text{Me}(30)$	49.1 (<i>d</i>)	$\text{C}(3)$, $\text{C}(4)$, $\text{C}(6)$, $\text{C}(7)$, $\text{C}(9)$, $\text{C}(10)$, $\text{C}(19)$, $\text{C}(28)$
$\text{CH}_2(6)$	2.04–2.12 (<i>m</i>)	$\text{H-C}(5)$, $\text{H-C}(7)$	$\text{Me}(19)$, $\text{Me}(28)$, $\text{Me}(29)$	23.0	$\text{C}(4)$, $\text{C}(5)$, $\text{C}(7)$, $\text{C}(8)$, $\text{C}(10)$
$\text{H-C}(7)$	5.47 (<i>d</i> , $J = 6.2$)	$\text{CH}_2(6)$	$\text{CH}_2(6)$, $\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{Me}(30)$	120.0 (<i>d</i>)	$\text{C}(6)$, $\text{C}(9)$, $\text{C}(14)$
$\text{C}(8)$				142.9 (<i>s</i>)	
$\text{C}(9)$				145.9 (<i>s</i>)	
$\text{C}(10)$				37.4 (<i>s</i>)	
$\text{H-C}(11)$	5.37 (<i>d</i> , $J = 6.5$)	$\text{H}_\alpha\text{-C}(12)$, $\text{H}_\beta\text{-C}(12)$	$\text{H}_\alpha\text{-C}(1)$, $\text{H}_\beta\text{-C}(1)$, $\text{H}_\alpha\text{-C}(12)$, $\text{H}_\beta\text{-C}(12)$, $\text{Me}(19)$	116.5 (<i>d</i>)	$\text{C}(8)$, $\text{C}(10)$, $\text{C}(12)$, $\text{C}(13)$
$\text{H}_\alpha\text{-C}(12)$	2.17 (<i>d</i> , $J = 17.6$)	$\text{H-C}(11)$, $\text{H}_\beta\text{-C}(12)$	$\text{H-C}(11)$, $\text{H-C}(17)$, $\text{H-C}(21)$, $\text{Me}(30)$	35.6 (<i>t</i>)	$\text{C}(9)$, $\text{C}(11)$, $\text{C}(13)$, $\text{C}(14)$, $\text{C}(17)$, $\text{C}(18)$
$\text{H}_\beta\text{-C}(12)$	2.38 (<i>dd</i> , $J = 17.6, 6.5$)	$\text{H-C}(11)$, $\text{H}_\alpha\text{-C}(12)$	$\text{H-C}(11)$, $\text{Me}(18)$, $\text{H-C}(21)$		
$\text{C}(13)$				43.8 (<i>s</i>)	
$\text{C}(14)$				50.6 (<i>s</i>)	
$\text{H}_\alpha\text{-C}(15)$	1.38–1.45 (<i>m</i>)	$\text{H}_\beta\text{-C}(15)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H-C}(7)$, $\text{Me}(30)$ $\text{H}_\beta\text{-C}(16)$		31.5 (<i>t</i>)	$\text{C}(13)$, $\text{C}(14)$, $\text{C}(16)$, $\text{C}(17)$, $\text{C}(30)$
$\text{H}_\beta\text{-C}(15)$	1.63–1.69 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H-C}(7)$, $\text{Me}(18)$, $\text{H}_\beta\text{-C}(16)$	$\text{Me}(19)$, $\text{Me}(29)$		
$\text{H}_\alpha\text{-C}(16)$	1.87–1.94 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{H}_\alpha\text{-C}(22)$, $\text{Me}(30)$ $\text{H}_\beta\text{-C}(16)$, $\text{H-C}(17)$		26.8 (<i>t</i>)	$\text{C}(13)$, $\text{C}(14)$, $\text{C}(15)$, $\text{C}(17)$, $\text{C}(20)$
$\text{H}_\beta\text{-C}(16)$	1.32–1.39 (<i>m</i>)	$\text{H}_\alpha\text{-C}(15)$, $\text{H}_\beta\text{-C}(15)$, $\text{Me}(18)$, $\text{H-C}(20)$, $\text{H}_\alpha\text{-C}(16)$, $\text{H-C}(17)$	$\text{H}_\beta\text{-C}(22)$, $\text{Me}(26)$		
$\text{H-C}(17)$	1.81–1.88 (<i>m</i>)	$\text{H}_\alpha\text{-C}(16)$, $\text{H}_\beta\text{-C}(16)$, $\text{H}_\alpha\text{-C}(12)$, $\text{H-C}(21)$, $\text{H-C}(20)$	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, $\text{Me}(30)$	49.9 (<i>d</i>)	$\text{C}(13)$, $\text{C}(14)$, $\text{C}(16)$, $\text{C}(18)$, $\text{C}(20)$, $\text{C}(22)$
$\text{Me}(18)$	0.62 (<i>s</i>)		$\text{H}_\beta\text{-C}(12)$, $\text{H}_\beta\text{-C}(15)$, $\text{H}_\beta\text{-C}(16)$, $\text{Me}(19)$, $\text{H-C}(20)$	16.8 (<i>q</i>)	$\text{C}(12)$, $\text{C}(13)$, $\text{C}(14)$, $\text{C}(17)$

Table 3 (cont.)

	$\delta(\text{H})$	$^1\text{H}, ^1\text{H-COSY}$	NOE	$\delta(\text{C})$	HMBC
Me(19)	0.98 (s)		$\text{H}_\beta\text{-C}(1)$, $\text{CH}_2(6)$, $\text{H-C}(11)$, $\text{H}_\beta\text{-C}(15)$, Me(18), Me(29)	22.7 (q)	C(1), C(5), C(9), C(10)
H-C(20)	1.87 (s)	H-C(17), H-C(21), $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$	$\text{H}_\beta\text{-C}(16)$, Me(18), $\text{H}_\beta\text{-C}(23)$	47.8 (d)	C(13), C(16), C(17), C(21), C(22)
H-C(21)	3.74 (t, $J=7.4$)	H-C(20), H-C(24)	$\text{H}_\alpha\text{-C}(12)$, $\text{H}_\beta\text{-C}(12)$, H-C(17), Me(26)	79.2 (d)	C(20), C(24), C(25)
$\text{H}_\alpha\text{-C}(22)$	1.25–1.27 (m)	H-C(20), $\text{H}_\beta\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	H-C(17), H-C(21), $\text{H}_\beta\text{-C}(22)$, $\text{H}_\beta\text{-C}(23)$	24.5 (t)	C(20), C(21), C(23), C(24)
$\text{H}_\beta\text{-C}(22)$	1.65–1.71 (m)	H-C(20), $\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$, H-C(24), Me(26)		
$\text{H}_\alpha\text{-C}(23)$	1.29–1.37 (m)	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$, $\text{H}_\beta\text{-C}(23)$, H-C(24)	H-C(17), $\text{H}_\beta\text{-C}(22)$	27.7 (t)	C(20), C(21), C(22), C(24), C(25)
$\text{H}_\beta\text{-C}(23)$	1.80–1.87 (m)	$\text{H}_\alpha\text{-C}(22)$, $\text{H}_\beta\text{-C}(22)$, $\text{H}_\alpha\text{-C}(23)$, H-C(24)	H-C(20), $\text{H}_\beta\text{-C}(22)$, Me(26)		
H-C(24)	1.86–1.94 (m)	H-C(21), $\text{H}_\alpha\text{-C}(23)$, $\text{H}_\beta\text{-C}(23)$	H-C(21), Me(27)	57.8 (d)	C(21), C(23), C(25), C(26), C(27)
C(25)				73.7 (s)	
Me(26)	1.22 ^a (s)		$\text{H}_\beta\text{-C}(22)$, $\text{H}_\beta\text{-C}(23)$, Me(24)	24.1 (q)	C(24), C(25), C(27)
Me(27)	1.24 ^a (s)		H-C(21)	30.8 (q)	C(24), C(25), C(26)
Me(28)	1.00 (s)		H-C(3), H-C(5), $\text{H}_\alpha\text{-C}(6)$, Me(29)	28.1 (q)	C(3), C(4), C(5), C(29)
Me(29)	0.88 (s)		$\text{H}_\beta\text{-C}(6)$, $\text{H}_\beta\text{-C}(15)$, Me(19), Me(28)	15.8 (q)	C(3), C(4), C(5), C(28)
Me(30)	0.91 (s)		H-C(5), H-C(7), $\text{H}_\alpha\text{-C}(12)$, $\text{H}_\alpha\text{-C}(15)$, H-C(17)	25.63 (q)	C(8), C(13), C(14), C(15)

^a) Assignments may be reversed.

2947, 1456, 1372, 1172, 1026. ^1H - and ^{13}C -NMR: Table 1. EI-MS: 458 (52, M^+), 443 (33, $[M - \text{Me}]^+$), 425 (100, $[M - \text{Me} - \text{H}_2\text{O}]^+$), 407 (96), 389 (13), 314 (8), 299 (44). HR-EI-MS: 458.3763 (M^+ , $\text{C}_{30}\text{H}_{50}\text{O}_3^+$; calc. 458.3760).

Inonotsutriol B (= (3 β ,21R,24R)-21,24-Cyclolanost-8-ene-3,21,25-triol = (3 β ,5 α ,17 β)-17-[(1R,2R,3R)-2-Hydroxy-3-(1-hydroxy-1-methylethyl)cyclopentyl]-4,4,14-trimethylandrosta-8-en-3-ol; **2**): Colorless crystals. M.p. 235–237° (from MeOH/CHCl₃). $[\alpha]_{\text{D}}^{20} = +40.3$ ($c=0.18$, CHCl₃). IR (KBr): 3434 (OH), 2942, 1653, 1457, 1373, 1157, 1030. ^1H - and ^{13}C -NMR: Table 2. EI-MS: 458 (48, M^+), 443 (27, $[M - \text{Me}]^+$), 425 (100, $[M - \text{Me} - \text{H}_2\text{O}]^+$), 407 (69), 389 (10), 383 (20), 314 (13). HR-EI-MS: 458.3759 (M^+ , $\text{C}_{30}\text{H}_{50}\text{O}_3^+$; calc. 458.3760).

Inonotsutriol C (= (3 β ,21R,24S)-21,24-Cyclolanosta-7,9(11)-diene-3,21,25-triol = (3 β ,5 α ,17 β)-17-[(1R,2R,3S)-2-Hydroxy-3-(1-hydroxy-1-methylethyl)cyclopentyl]-4,4,14-trimethylandrosta-7,9(11)-dien-3-ol; **3**): Colorless crystals. M.p. 213–215° (from MeOH/CHCl₃). $[\alpha]_{\text{D}}^{20} = +72.6$ ($c=0.21$, CHCl₃). UV (EtOH): 232 (12000), 237 (14500), 245 (9000). IR (KBr): 3675 (OH), 2950, 1653, 1559, 1374, 1158, 1028.

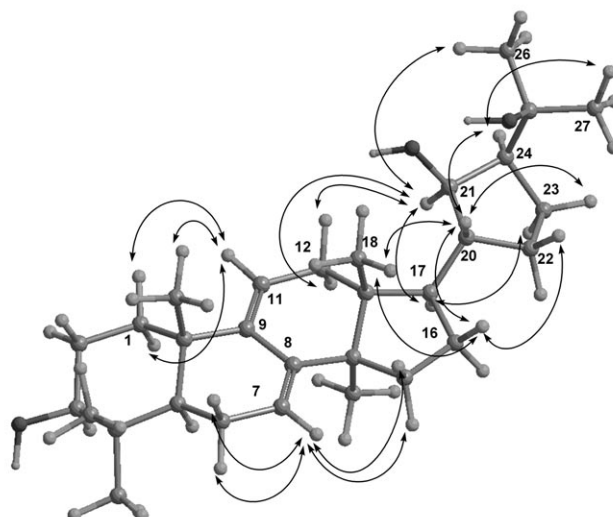
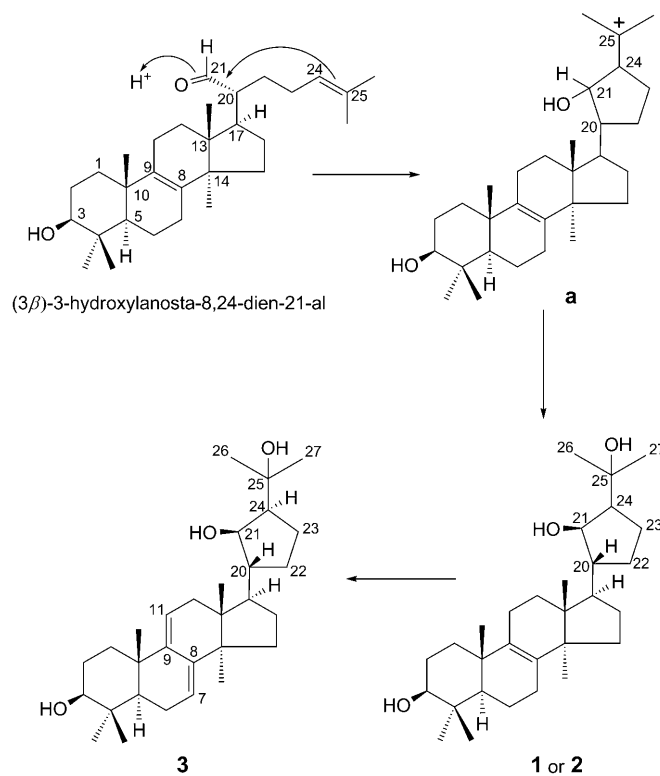


Fig. 3. Key NOE correlations for **3**

Scheme. Plausible Biogenetical Pathway to Compounds **1–3**



¹H- and ¹³C-NMR: Table 3. EI-MS: 456 (19, *M*⁺), 438 (100, [*M* – H₂O]⁺), 423 (14, [*M* – Me – H₂O]⁺), 405 (8), 356 (20), 312 (34), 297 (16). HR-EI-MS: 456.3607 (*M*⁺, C₃₀H₄₈O₃⁺; calc. 456.3604).

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